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DESIGN AND CONSTRUCTION OF A TEST APPARATUS FOR EVALUATING SPONTANEOUS COMBUSTION SUSCEPTIBILITY OF CANADIAN COALS - PHASE I

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Submitted by

ASSOCIATED MINING CONSULTANTS LTD.

with

GEOTECHnical Resources Ltd.

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DESIGN AND CONSTRUCTION OF A TEST APPARATUS FOR EVALUATING SPONTANEOUS COMBUSTION SUSCEPTIBILITY OF CANADIAN COALS - PHASE I

Final Report

by

ASSOCIATED MINING CONSULTANTS LTD.

with

GEOTECHnical Resources Ltd.

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SPONTANEOUS COMBUSTION TEST APPARATUS

PHASE I

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SPONTANEOUS COMBUSTION TEST APPARTUS
PHASE I

EXECUTIVE SUMMARY

The CANMET Surface Mining Laboratory, Devon, requires a computer controlled multi-sample test apparatus to carry out spontaneous combustion susceptibility tests on Canadian coals.

The exothermic reaction mechanisms between oxygen, water and coal which can result in self heating are described. The factors affecting spontaneous combustion include intrinsic parameters of the coal itself such as rank, moisture, oxygen and sulphur contents, particle size, petrographic composition, methane adsorbed and physical characteristics such as porosity, hardness, thermal conductivity and specific heat. Extrinsic factors including air flow rates and humidity, geologic setting and mining practice can have a major impact on whether spontaneous heating actually occurs.

There is no universally accepted standard method to test for the susceptibility of coal to spontaneous combustion. Many different methods have been tried with variations within each. Laboratory tests include isothermal, adiabatic, paced adiabatic, oxygen absorption, ignition temperatures, chemical methods, differential thermal analysis and gravimetric analysis. The wide range of apparatus used is described.

The report outlines current worldwide test procedures. No consensus is apparent apart from the fact that, in general, coal operators use the simpler empirical tests.

Comparison between test methods depends on the information required because each test is suited to study a particular aspect of the process. The

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purpose of the apparatus should be carefully reviewed prior to the Phase II commitment as this will affect the final design. For CANMET, the requirement of a multi-sample apparatus precludes the use of adiabatic methods. An apparatus which can operate in a number of test modes is recommended, so that isothermal, oxygen absorption, ignition temperatures, and differential thermal analysis test procedures can all be performed.

The functional requirements and system configuration for the proposed apparatus are outlined.

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APPAREIL À ANALYSER LE CHARBON POUR LA COMBUSTION SPONTANÉE
PHASE I

SOMMAIRE

Le laboratoire de recherches pour mines à ciel ouvert de CANTME, à Devon, a besoin d'un appareil, contrôlé par un ordinateur, destiné à analyser la susceptibilité des charbons candiens à la combustion spontanée. Cet appareil pourrait faire l'analyse de plusieurs échantillons à la fois.

Les mécanismes de réaction exothermique entre l'oxygène, l'eau et le charbon qui peuvent déclencher l'inflammation spontanée sont décrits dans la présente étude. Les facteurs ayant rapport à la combustion spontanée incluent les paramètres intrinsèques au charbon même soit le rang, l'humidité, la teneur en sourfre et en oxygène, la granulométrie, la composition pétrographique, le méthane adsorbé ainsi que des caractéristiques physiques telles que la porosité, la dureté, la conductivité thermique et la chaleur spécifique. Les facteurs extrinsèques y compris les débits d'air, l'humidité, le cadre géologique et les pratiques d'exploitation minière peuvent avoir un effet important sur le fait que la combustion spontanée se produira ou non.

Il n'y a pas de méthode modèle universellement acceptée pour analyser la susceptibilité du charbon à la combustion spontanée. Plusieurs méthodes différentes ont été essayées. Les méthodes utilisées en laboratoire comprennent la méthode isothermique, la méthode adiabatique, la méthode adiabatique graduelle, la méthode d'absorption de l'oxygène, la méthode des températures d'inflammation, les méthodes chimiques, les analyses thermiques différentielles et les analyses gravimétriques. Cette étude décrit le grand assortiment d'appareils utilisés.

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Le rapport trace aussi les grandes lignes des méthodes actuelles utilisées de par le monde. On n'y voit pas de consensus excepté qu'en général, l'industrie du charbon emploie les tests empiriques les plus simples.

La comparaison entre les méthodes d'analyses dépend de l'information qu'on veut obtenir parce que chaque analyse est adaptée à l'étude d'un aspect particulier du procédé. Le but ultime de l'appareil devrait être attentivement examiné avant de s'engager dans la Phase II puisque cela affectera le dessin final. En autant que CANTME est concerné, la nécessité d'avoir un appareil qui peut effectué des analyses sur plusieurs échantillons à la fois exclut l'emploi de méthodes adiabatiques.

Un appareil qui peut utiliser plusieurs procédés est recommendé afin que la méthode isothermique, la méthode d'absorption de l'oxygène, la méthode des températures d'inflammation et les analyses thermiques différentielles puissent toutes être employées.

Cette étude esquisse aussi l'aspect général et le fonctionnement de l'appareil proposé.

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SPONTANEOUS COMBUSTION TEST APPARATUS
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SECTION 1 - INTRODUCTION

1.1 GENERAL

Spontaneous combustion resulting from self-heating of coal can lead to fires in highwalls of surface mines, on trains, in storage piles and presents a potentially fatal hazard underground. It can provide the ignition source for explosive mixtures and the source of toxic and flammable gases.

Extensive research studies over the past 100 years have demonstrated that one of the most important factors in spontaneous heating is the susceptibility of the coal itself, with low rank coals being more susceptible than high rank coals. Additional factors that affect the rate at which spontaneous combustion will occur include changes in moisture content of the coal, air flow rate and its humidity, particle size, temperature, pyrite content, geologic factors and mining practice. Given the right conditions, almost every coal will self-heat.

A knowledge of the relative susceptibility of coals to spontaneous combustion is useful in assessing the precautions necessary while selecting mining methods and surface handling procedures, and in choosing product specifications. A data-base for Canadian coals is required against which a comparison can be made for new coal seams and differing product specifictions.

The CANMET Surface Mining Laboratory, Devon, Alberta, have an ongoing research program into spontaneous combustion. To enhance this program CANMET require the development of a computer controlled automated multi-sample test apparatus for carrying out

spontaneous combustion susceptibility tests on Canadian coals. This will be carried out in three phases:

Phase I - Historical Review and Functional Definition
Phase II - Detailed Design
Phase III - Construction

Associated Mining Consultants Ltd. (AMCL), with the support of GEOTECHnical Resources Ltd. have been contracted to implement the Phase I Study.

1.2 TERMS OF REFERENCE

The terms of reference for the overall project are summarized as follows:

PHASE I

1. Carry out an in depth review of methods currently being used for determining the spontaneous combustion susceptibility of coals in Canada and abroad.
2. List relative merits and demerits of each method and their possible applications to Canadian Coals.
3. Based on the survey, make recommendations for a multi-sample system and define the functional requirements of an automated apparatus.
4. Evaluate various system options for meeting the functional requirements and select the most appropriate configuration for the proposed test apparatus.
5. Prepare a report.

PHASE II

1. Prepare a detailed design of the proposed spontaneous combustion test apparatus.

2. Select and prepare a list of components required to build the test system which must include specifications, availability and cost.

3. Prepare a draft manual for calibration and maintenance procedure for the test apparatus.

4. Make a detailed theoretical evaluation of the proposed system highlighting the limitations, if any.

5. Prepare a comprehensive report.

PHASE III

1. Procure all the necessary parts for the construction of the approved apparatus.

2. Make a prototype test apparatus and conduct necessary tests to confirm specifications.

3. Conduct experiments to prove the suitability of the test apparatus for carrying out spontaneous combustion studies.

4. Using the prototype test apparatus, carry out experiments to establish repeatability, accuracy and reproducibility of results.

5. Prepare a comprehensive operations and maintenance manual.

6. Complete fabrication of the test equipment and install the same at Coal Research Laboratory premises at Devon, Alberta.

7. Provide adequate spares and consumables for a period of at least one year after the delivery date.

8. Submit a Final Report.

The results of the Phase I work only are included in this report.

1.3 STUDY TEAM

The study was carried out under the direction of Alan L. Craven, Project Manager, with contributions by Jim Lucas and Ed Codding (GEOTECH).

SPONTANEOUS COMBUSTION TEST APPARATUS

PHASE I

SECTION 2 - SPONTANEOUS COMBUSTION

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SECTION 2 - SPONTANEOUS COMBUSTION

2.1 GENERAL

Spontaneous heating of coal is an extremely complex process which is dependent not only on the chemical and physical properties of the coal itself, but also on the environment in which the coal is placed.

The chemical aspects of the spontaneous combustion of coal are not well understood because of the complex composition of coals and the different heterogeneous surface reactions that can be included. However, it is generally agreed that coal begins to oxidize as soon as it comes into contact with oxygen and the reaction is exothermic. Additionally, moisture readsorption can produce heat. If the heat evolved is greater than the heat dissipated to the surroundings, then there will be a rise in temperature of the coal and a consequent acceleration of the exothermic reaction, until the coal ignites, providing there is a sufficient availability of oxygen. Self-heating can occur with any coal given the right conditions, but all coals are not equally susceptible. The purpose of the proposed test apparatus is to measure the relative susceptibility to spontaneous combustion of different coals.

2.2 REACTION MECHANISM

Coal begins to oxidize as soon as it comes into contact with oxygen. At low temperatures stable coal/oxygen complexes form with the reaction being:

Coal + Oxygen = Coal/Oxygen Complex + Heat

The coal/oxygen compounds will be per-oxy complexes which start to break down at higher temperatures with the reaction being.

$$\text{Coal/Oxygen Complex} = CO + CO_2 + H_2O + \text{Heat}$$

The rate of oxidation approximately doubles for every 10°C increase in temperature and so the reactions accelerate until ignition occurs. As the temperature increases hydrogen and other hydrocarbons are given off. Typical curves are shown in Figure 2-1. Some workers believe that oxygen is adsorbed onto the surface of coal below 50°C with chemisorption of oxygen above this temperature. However, the general concensus appears to be that chemisorption occurs at temperatures as low as -5°C. The breakdown of the coal/oxygen compounds is normally considered to occur at temperatures above 80°C, although some research has indicated that breakdown to carbon dioxide and carbon monoxide can be identified as low as 42°C. Clearly the oxygen adsorption, chemisorption reactions overlap with chemisorption becoming dominant above 0°C. Likewise, while formation of coal/oxygen complexes continues to 80°C and above, their breakdown commences at much lower temperatures.

The chemical heat release is thought to follow the Arrhenius Law where the self-heating rate under adiabatic conditions is:

$$\frac{dT}{dt} = ke^{\frac{-E}{RT}}$$

or:

$$\ln \frac{dT}{dt} = \frac{-E}{RT} + \ln k$$

where:

T	=	temperature
t	=	time
E	=	activation energy
R	=	molar gas constant
k	=	rate constant

The slope of a plot of ln $\frac{dT}{dt}$ against $\frac{1}{T}$ from experimental results is equal to $\frac{E}{R}$, allowing k to be calculated. The slope changes in the 80°C - 120°C range so calculation should be considered above and below this range. Figure 2-2 shows a typical Arrhenius plot.

The rate constant will vary according to the oxygen content of the gas, average particle size of the sample tested, humidity of gas stream, etc., as well as due to the chemical and physical properties of the coal itself (Figures 2-3 and 2-4).

The heat of wetting is an important contributor to spontaneous combustion of low rank coals, and the heat contributed accelerates the formation of coal/oxygen complexes. When dry coal is wetted, or moisture readsorbed, heat is generated. For coals below equilibrium moisture, a 1% increase in moisture content will increase the temperature of the coal by about 22°C. Below about 80°C, the heat generated by the reaction of dry coal and moisture is greater than the heat produced by oxidation.

Two mechanisms of heating with water are possible, chemisorption and condensation. The heat of condensation is thought to be significantly higher than the heat of chemisorption, therefore moisture readsorption produces more heat than wetting the coal with liquid water.

A detailed literature review of the reaction mechanism is given by Bachelor and Majumdar (1986) in CANMET Report 0SG83-00109.

2.3 FACTORS AFFECTING SPONTANEOUS HEATING

A number of factors affect the rate of spontaneous heating in oxidation of coal.

2.3.1 Rank

The rank of a coal is probably the most important factor in assessing a coal's susceptibility to spontaneous heating. As the rank of coal decreases, the rate of oxidation increases and thus lignites and sub-bituminous coals are most susceptible to spontaneous heating and anthracites the least. The oxygen and carbon contents of coal which are rank related are also often related to susceptibility.

There are fairly good relationships between the rate of oxidation of a coal and its rank related characteristics, however, there are always some anomolies. One part of a seam can be more liable to spontaneous heating, and the same seam can react differently in different locations. Other factors must be considered including inherent features such as hardness, petrographic composition and porosity, and external factors such as the surrounding environment.

2.3.2 Moisture

The role of moisture in spontaneous heating is very complex and is particularly important when considering lower rank coals.

Water can be adsorbed, chemically bound or mechanically mixed with the coal and each case has a different effect on oxidation.

Water mechanically mixed with coal slows down the oxidation process, presumably because the access of oxygen to the surface of the coal is blocked.

Drying coal is an endothermic reaction and the loss of heat by evaporation of moisture from the surface of wet bituminous coal is three to four times greater than any heat of oxidation.

However, if a coal is dried, then more oxidative sites are exposed and the coal becomes more reactive.

Moisture can be absorbed onto dry coal in an exothermic reaction. Absorption of water provides some heat but if the reaction takes place from water vapour the heat evolved is significantly greater, since it includes the latent heat of condensation of water.

It has been demonstrated that a rise of temperature of between 20°C - 50°C can be achieved by passing moisture laden inert gas over a dried coal where little rise in temperature is achieved when passing dry oxygen over the same coal.

Any tests for susceptibility of coal to oxidation must provide measurement and control of the humidity of the oxidizing environment and be related to the moisture content of the coal sample itself.

2.3.3 Oxygen

The oxygen content of a coal (dry mineral matter free basis) is an indication of rank with higher oxygen coals being lower rank and most reactive.

The relationship between the rate of oxidation of a coal and the oxygen concentration of surrounding atmosphere has been found to be of the first order:

$R = kp^n$

where

R = rate of oxygen absorption
k = constant
p = partial pressure of oxygen in oxidizing medium
n = order of reaction with respect to oxygen.

The factor 'n' was found by some workers to be equal to 0.5 while others measured 0.66.

The significance is that oxygen contents must be measured and controlled in any tests for susceptibility.

2.3.4 Particle Size

Particle size has an inverse relationship to the rate of oxidation of coal. The smaller the coal the greater is the exposed surface area and the greater is the tendency towards spontaneous heating.

Oxidation occurs not only on the outer surface of the coal particle but also on the inner surfaces of the coal pores. Some coals have an extensive intercommunicating structure of fine tunnels that are relatively permeable to air and provide sites for oxidation. In other coals such as anthracite, such structures hardly exist.

The increase in oxidation rate for a particular coal with respect to particle size is given by the equation:

$R = ks^n$

where

R = rate of oxygen absorbtion
k = constant
s = surface area
n = order of reaction with respect to surface area.

The factor 'n' has been determined by various researchers to be from 0.33 to as high as 0.65. Using the lower figure means a 1000-fold increase in surface area only produces a 10-fold increase in oxidation rate.

It appears that low temperature oxidation takes place within the coals as well as on the surface. The rate of oxidation increases with decrease in particle size until a size is reached at which any further increase in oxidation rate is very small. It is suggested that at this size (50 microns) the oxygen can penetrate the coal completely.

In testing for susceptibility the particle size of the sample must be controlled if comparable results are to be obtained.

2.3.5 Temperature

The rate of coal oxidation is a direct function of temperature; the higher the temperature the faster the rate at which coal reacts with oxygen. This is particularly important in areas where heat generated by oxidation accumulates, further accelerating the rate of oxidation.

A rise in temperature of 10°C can increase the rate of oxidation from 1.2 to 2.3 times, with the factor dependent on rank (lowest value for anthracite). Since the oxidation produces heat for a temperature rise, in the absence of cooling the reaction is self-accelerating.

As the temperature increases the chemical reactions that take place change as described in paragraph 2.2.

Measurement and control of heat and temperature are fundamental to many of the procedures for testing for susceptibility.

2.3.6 Air Flow Rates

The air flow rate is an important factor because it provides oxygen for oxidation of the coal and dissipates the heat generated by oxidation. Where there is only a small amount of available oxygen the rate of oxidation can be limited by this factor and there is little rise in temperature. If air quantities are very large any heat produced is carried away so that again the temperature does not rise and oxidation remains at a low level. In between these two limits there is a state where the amount of air available is sufficient to promote oxidation but not sufficient to carry away the heat formed, so there is an accelerating rate of oxidation until ignition occurs.

As previously discussed, the humidity of the air flow is important. If the partial pressure of water vapour in the air flow is lower than that of the moisture in the coal sample, then moisture will evaporate from the sample with a consequential cooling effect. Conversely, if the partial pressure of the water vapour in the air flow is greater than in the sample, water will be readsorbed in an exothermic reaction increasing the sample temperature.

2.3.7 Sulphur and Other Minerals

Sulphur in the form of pyrites (FeS_2) or pyrrhotite (FeS) is considered to play a minor role in the susceptibility of coal to self-heating although french researchers believe it to be a major factor in the onset of spontaneous combustion in some of their mines. The heat of oxidation can increase the coal temperature thus increasing its oxidation rate. More importantly perhaps, the pyrite and pyrrhotite swell as they oxidize and break down the coal to a smaller size, thereby assisting the diffusion of oxygen and increasing the exposed surface area of the coal.

Many other chemicals affect the rate of oxidation to some extent, either accelerating or retarding it. Some alkalis and acids can act as accelerators, while borates, calcium chloride and some wetting agents act as retardants. Most of these chemicals are present in very small amounts in coal seams, but attempts have been made to limit spontaneous combustion by their addition to coal either underground or in stockpiles.

2.3.8 Petrographic Composition

Petrographic composition plays a significant role in the coal oxidation process. The permeability, particle size and internal surface area will vary with the petrographic components.

Fusinite used to be considered the most dangerous maceral, but it is concluded this is due to its physical form with its large surface area.

Work by Chamberlin indicated that exinite is much more reactive than vitrinite and inertite, particularly above 70°C. Thus, a maceral count and reflectance measurement together with rank can be correlated, to some degree, with susceptibility to spontaneous heating. Maceral content may explain some of the anomalies of oxidation characteristics of coals of the same rank from different parts of the same seam or different seams.

2.3.9 Methane

There is some experimental evidence that adsorbed methane may inhibit the initial oxidation reactions since while the methane is desorbing, oxygen is inhibited from entering the coal substance. The methane essentially creates an inert atmosphere near the surface of the coal. Coal from areas where methane could have

desorbed such as near surface or faults in shear zones, or below permeable strata will, therefore, be more susceptible to oxidation.

2.3.10 Ageing

Coal begins to oxidize as soon as it is exposed to oxygen. Unless it is broken or dried to provide new oxidative sites, then the reaction rate will slow down. Thus, older coal is normally safer than freshly mined coal from a self-heating point of view. In highly gassy coals where methane desorption initially retards oxidation, as the emission of methane slows more surface becomes exposed to oxidation and the oxidation rate increases.

2.3.11 Physical Properties

Physical properties such as porosity, hardness, thermal conductivity and specific heat can affect the rate of oxidation.

Porosity affects the area exposed to oxidation with low rank coals being generally more porous. Coals from same rank can vary in porosity.

Hardness, measured by friability or grindability, affects the ease with which coal breaks down to smaller and more oxidizable sizes.

Specific heat determines the rise in temperature for a given heat input and has a constant value of around 0.2 for most coals.

Thermal conductivity, a measure of the rate of transfer of heat over unit area for unit temperature gradient is relatively low for coal. Coals with lower thermal conductivities are more susceptible to spontaneous heating since heat is dissipated more slowly.

These thermal properties affect temperature rise but their effects are relatively minor.

2.3.12 Geologic Factors

The presence of faults in the coal seam may contribute to spontaneous heating by allowing air and water to migrate into the coal seam. Zones of weakness around faults also allow air leakage into the coal mass. When the coal seam under shallow cover is mined, cracks and fissures may develop in the coal and adjacent strata. Air and water from the surface can gain access to the coal and increase the potential for spontaneous heating.

2.3.13 Mining Practice

Several factors in the mining method (both surface and underground) and in the method of stockpiling and handling, can increase the potential for spontaneous heating. Areas where fine coal particles accumulate, especially gob areas, present a hazard because of the large coal surface available for oxidation. Air leakage around and through fissured pillars and into abandoned areas of the mine allow coal to oxidize and also allow generated heat to accumulate. Changes in ventilation, either intentional or accidental, may cause air leakage or may suddenly bring moist air into contact with dry coal.

2.3.14 Summary

Although all the above factors affect spontaneous heating of coal, rank and changes in moisture content are apparently the most important. Any tests for susceptibility must be empirical because of the heterogeneous nature of coal and the many complex chemical and physical factors which affect this characteristic.

Ideally, the properties of the coal in terms of proximate and ultimate analysis, rank and petrographic composition, should be known for any coal sample tested.

The following parameters should be measured and controlled in any test:

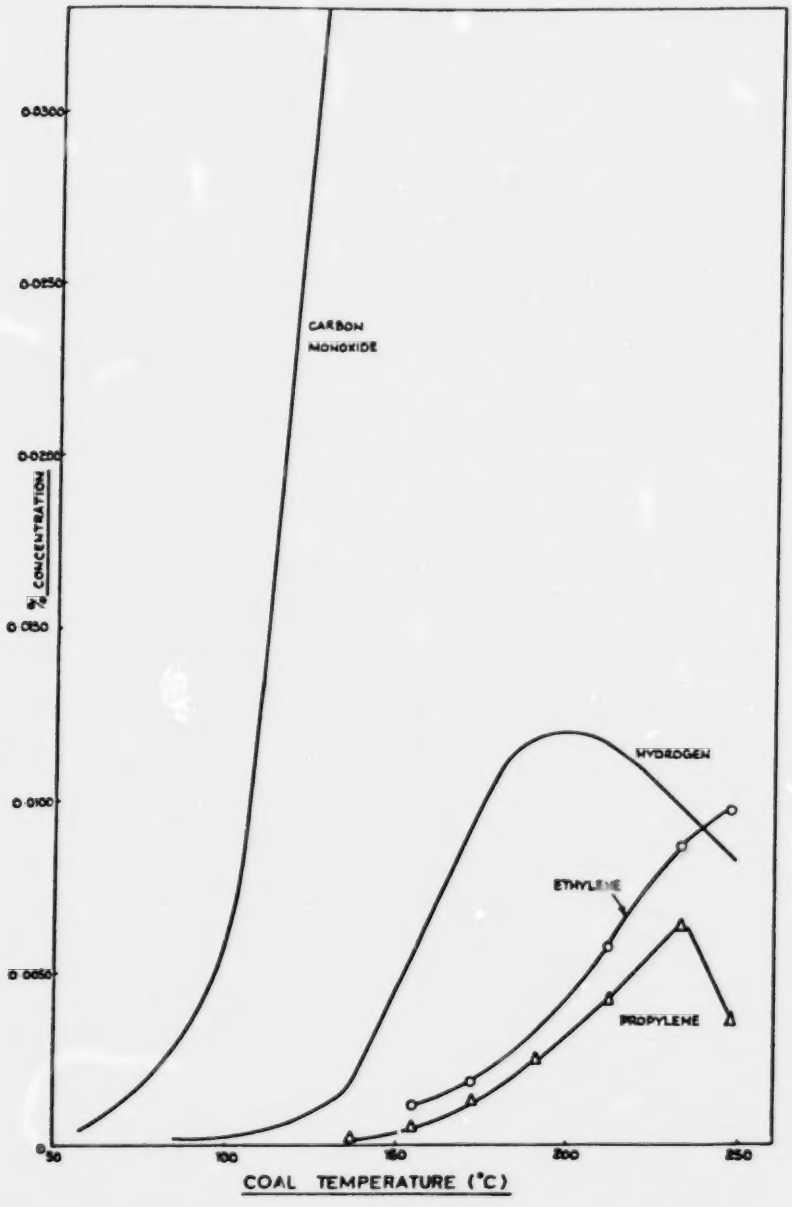
- Moisture content of sample
- humidity of inlet and outlet gas
- oxygen content of inlet/outlet gas
- control of partial pressure of oxygen
- pressure of gas
- particle size of sample
- temperature of sample and surroundings
- air/gas flow rates.

These changes to be monitored could include:

- Gas composition
- temperature of sample and surroundings
- sample weight.

FIGURE 2-1
SPONTANEOUS COMBUSTION TEST APPARATUS

A TYPICAL DYNAMIC OXIDATION TEST
GAS CONCENTRATION vs TEMPERATURE

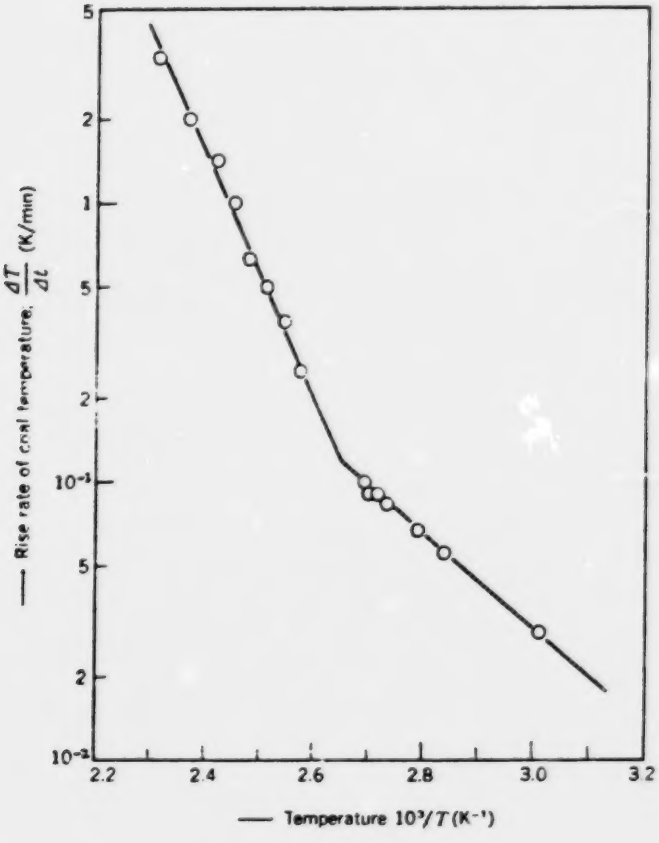


Source: Chamberlain, 1970.

FIGURE 2-2

SPONTANEOUS COMBUSTION TEST APPARATUS

ARRHENIUS PLOT



Source: Onitsuka and Watanabe, 1982.

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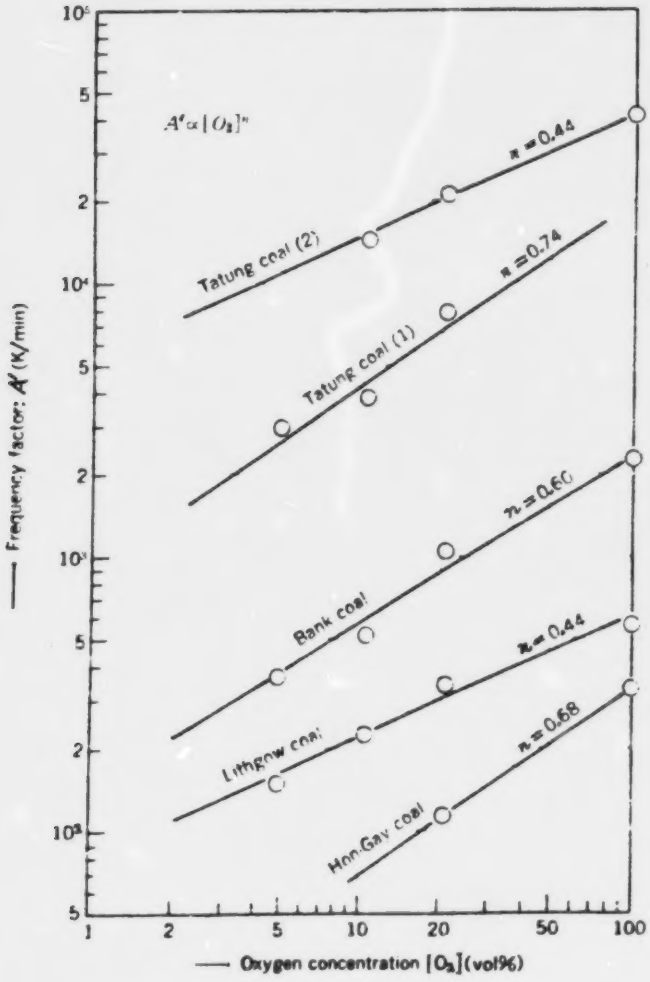
FIGURE 2-3
SPONTANEOUS COMBUSTION TEST APPARATUS

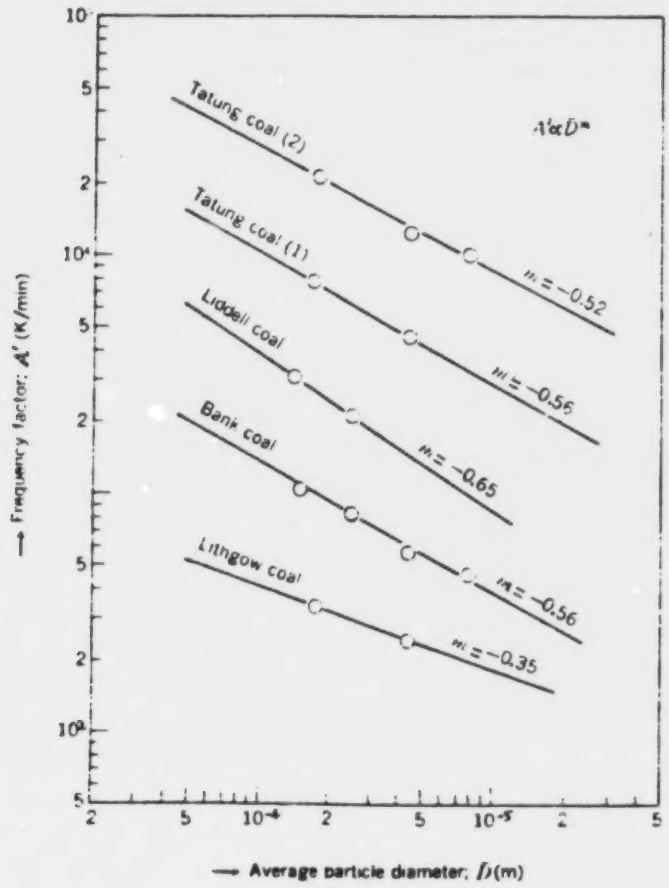
EFFECT OF OXYGEN CONCENTRATION ON REACTION RATE



Source: Onitsuka and Watanabe, 1982

FIGURE 2-4
SPONTANEOUS COMBUSTION TEST APPARATUS

EFFECT OF PARTICLE DIAMETER ON REACTION RATE



Source: Onitsuka and Watanabe, 1982

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3-3 Schematic of Adiabatic Heating Apparatus

3-4 British Coal Adiabatic Apparatus Schematic

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SECTION 3 - TESTS FOR SUSCEPTIBILITY

3.1 INTRODUCTION

All coals begin to oxidize once they are mined, and given the right conditions will self-heat. However, coals show considerable differences in their liability to spontaneous combustion and a laboratory test is desirable which determines their relative oxidation rates. This knowledge can assist in decisions on the precautions necessary when planning a new mine or determining product specifications. In practice, mining or storage factors may be more dominant in determining whether spontaneous combustion will occur in a given situation. The coal reactivity is, nevertheless, very important.

Many different methods have been used to determine relative susceptibility of coal to spontaneous combustion and there are numerous variations on each method described in literature. In this section we describe some of these methods and the apparatus used.

3.2 STATIC ISOTHERMAL METHOD

This was the earliest attempt to devise a laboratory method for assessing the liability of coals to spontaneous combustion. The rate at which coal absorbs oxygen and gives off various gases is measured at constant temperature. In this method, a coal sample is placed in a large bath held at constant temperature. Heat generated in the coal sample, by oxidation or wetting is dissipated in the relatively large heat-sink.

In the earliest tests in the UK by Winmill and Graham, a series of bottles (usually 6), each fitted with an airtight bung and tap containing 5 g of glass wool, 1 mL of distilled water and 10 g of freshly ground coal to be tested, are placed in a thermostat at 30°C. A bottle is then removed at intervals, from 3 to 96 hours, and the gas in the bottle analysed, allowing a calculation to be made of the oxygen absorbed per gram of coal.

Between about 1913 and 1920, experiments on the rate of absorption of oxygen at 30°C (86°F) were carried out and confirmed earlier published results by Winmill and Graham that absorption was rapid at first, but gradually approached zero. Time-absorption curves were published for 40 British coals, whose reputation for being the cause of spontaneous fires varied greatly. It was found that coals not liable to 'fire' absorbed less than 200 mL of oxygen per 100 g of coal during 96 hours at 30°C (designated as "A96"), and those liable to 'fire', more than 200 mL in the same time.

The parameters of particle size, temperature, oxygen content of the oxidizing atmosphere, moisture content of sample and humidity of atmosphere can differ in variations of the test. The atmosphere may be flowing or static.

USBM (RI 8474) describes tests using dry air at 25°C. Coal samples were crushed and stored in a nitrogen atmosphere. Most of the experiments were in a 250 mL vessel with 50 g samples of freshly ground coal in 10-20 mesh (2-0.85 mm). The procedure consisted of sealing the sample in an Erlenmayer flask equipped with a pressure transducer and sampling the gases for extended periods to determine CO, CO_2 and CH_4 emissions and the O_2 absorption. The gas samples were withdrawn through a vessel port by hyperdermic syringe. The

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gases were analysed by conventional gas chromatographic methods that could detect CO concentrations down to 5 ppm and O_2 differences of 500 ppm. The experiments were carried out on both dried and undried samples. Samples were dried by exposing them to flowing nitrogen at 70°C for 24 hours.

An improved isothermal type calorimeter has been used by CSIRO, Australia as reported by Nordon, et al (J. Phys. E: Sci. Instrum. Vol.18, 1985 see Appendix A). The system allows the heat of reaction and rate of reaction to be determined simultaneously and maintains stability for a period of several weeks.

Gas for the reaction is pumped by peristaltic pump into the calorimeter and the flow rate and total gas flow determined from motor revolutions. After passing through the calorimeter, the chemical composition of the gas stream is analysed by automated gas chromatography. The pumping rate is adjusted so that reaction with the coal results in only a small drop in oxygen concentration (for air, say 1% to 2%) and hence the concentration difference between inlet and outlet streams together with the flow rate permit calculation of the amount of oxygen which has combined with the coal. By permitting only a small drop in the concentration to occur, the mean concentration of oxygen taking part in the reaction is known within reasonable limits.

A characteristic of the system is the slow displacement time for the gas. At a low flow rate of, say, 3 $mm^3\ s^{-1}$ it takes longer than 12 hours to change the concentration of oxygen in the calorimeter.

The calorimeter is based on the Calvet type in which the heat flux produced by the reaction is measured as a temperature difference across an air gap between concentric cylinders, the inner one holding

the sample and the outer one being essentially at a constant temperature.

The inner cylinder has a removable insert, also in the form of a hollow cylinder, which holds the coal sample. During operation fresh oxidising gas enters at the bottom of the cylinder, passes between the coal particles and leaves from the top via a tube to a gas chromatograph. Due to the very low flow rate used an even gas distribution over the coal (at right angles to the axis of the cylinder) is achieved by molecular diffusion.

The construction of the calorimeter is shown in Figure 3-1.

The successful operation of the system depends on the outer calorimeter block being held at steady temperature. Because of the high sensitivity of the thermopile and limitations inherent in the thermostat, the system is built up of two identical calorimeters with their thermopiles connected in opposition so that external fluctuations in temperature tend to be cancelled. The sensitivity of the calorimeter is about 10^{-6} watts/g coal. The two calorimeters are placed close together in a sand bath. The thermostat plays a key role in the operation of this type of calorimeter, particularly where the heat output of slow reactions is monitored over several weeks. The temperature of the air circulating in the oven has to be closely controlled to less than $\pm$ 1°C.

In a typical test, 40 g of crushed coal in the 3.35 - 0.85 mm size range is used to measure rate of oxygen fixation and heat evolution at, say, 55°C. It takes 24 hours for the thermostat, sand bath and calorimeters to reach thermal equilibrium and a number of days or weeks to complete the tests. This calorimeter is particularly suited to measuring oxygen absorption and reaction heats at near ambient temperatures.

Heemskerk reports that the Prins Maurits Laboratory in The Netherlands, has developed what he describes as an Isothermal Storage Test (IST).

In the Isothermal Storage Test (IST) the heat generated at constant temperature by reacting of decomposing substances is measured as a function of time. Performance of these measurements at a series of temperatures leads to a quantative understanding of the relation between the temperature and the heat generation of the substance under investigation. The IST is applicable to solids, liquids, pastes and dispersions.

The IST shown in Figure 3-2 consists of a large heat sink (an aluminum block) which is kept at a constant temperature. In the block are two holes with a heat flow meter (eg a Peltier element) at the bottom of each hole. Holders are placed on both heat flow meters. These holders are identical. One holder contains the sample, the other an inert substance.

The heat generated by the sample results in a voltage signal from the heat flow meter which is proportional to the heat flow. Random fluctuations in the heat flow are avoided by monitoring the voltage difference between both heat flow meters.

The stainless steel sample holder has a volume of 70 cm^3. The sample mass amounts to about 20 g. Measurements can be performed in the temperature range from -25°C to 147°C. Heat generations can be measured between the lower limit of 5 mW/kg and the upper limit of 4 W/kg with an accuracy of at least 30% in the lower range to 5% in the higher ranges.

3.3 OXYGEN ADSORPTION

This is similar to the isothermal method except that the coal sample temperature rises and is measured with thermocouples.

In the oxygen adsorption method, a coal sample is placed in a container and air and oxygen products are periodically removed and the amount of air or O_2 that must be added to maintain the system at constant pressure is used to estimate the amount of oxygen adsorbed. In the flow system, the flow rate and analysis of the effluent gas are used to estimate the amount of oxygen absorbed by the coal. The temperature increase per unit of oxygen consumed indicates the coal's potential for spontaneous heating. Alternatively, the heat generated is measured as opposed to temperature rise taking into account heat losses to the surroundings of the sample.

In a variation of this method, CANMET analyse the gases within the container after 96 hours. Up to that time, they measure the drop in pressure within the container.

3.4 ADIABATIC METHODS

In adiabatic calorimetry, the coal sample is placed in an insulated container and the system heated to a preselected temperature. When oxygen or air is passed through the sample, the temperature of the coal rises. The surrounding atmosphere is then heated to match the measured temperature of the sample. Thus, there is no heat loss to the surroundings and changes in temperature of the coal sample can be

accurately measured. The change in temperature of a coal in a given time, the time needed to reach a preselected temperature, the amount of heat generated per unit of time, or the quantity of gases desorbed or adsorbed at a certain time or temperature, can all be relative measures used in evaluating the spontaneous heating potential of the coal.

The true adiabatic method of testing, where the sample and its surroundings are maintained at the same temperature, more closely reflects what happens in actual conditions. However, reactions are slow at low temperatures, so the tests may take a long time (months) to complete. To speed up the process experiments can be started at higher temperatures ($70^{o}C+$). During build-up to these starting temperatures, dry nitrogen or other dry inert gases are used to prevent premature oxidation.

In the design of the adiabatic apparatus the key is the method by which the surroundings are kept at the same temperature as the sample. Different materials are used for the immediate surroundings, including air, water, glycerine, oil, or metal cores. Temperature control systems must be designed to maintain the surrounding temperature as close to the sample temperature as possible. The surrounding temperature must not exceed the sample temperature, otherwise a pull/push system of control develops and test results lose their value.

The apparatus used by USBM (RI 8474) is shown in Figure 3-3.

The calorimeter consists of an insulated oven chamber with three separate heaters, a 15 cm diameter Dewar vessel containing a sample oven (middle heater), and a stainless steel wire sample basket (7.6 cm in diameter by 7.6 cm high) suspended by a wire strand. Pre-heated air is brought into the calorimeter by passing it through an externally heated

line and the outer oven; the air enters near the bottom and slowly circulates up around the sample with the help of a magnetically controlled fan (<5 rmp). Iron-constantan thermocouples are installed at various locations for determining the sample and oven temperatures; sample/oven differential thermocouples are used for control purposes and for detection of self-heating. All thermocouples need to be simultaneously calibrated.

Thermocouple outputs are fed to an instrument console that is equipped with solid-state electronic components for programming the heating and for monitoring or controlling the sample and oven temperatures. These outputs are recorded continuously on millivolt recorders and spot-checked by use of a digital differential voltmeter. This system is sufficiently sensitive to detect temperature differences as small as 0.02°C and has a drift rate from electronic instability of about 0.05° per hour at 50°C. The calorimeter was also equipped with a load cell for monitoring sample weight changes. It has since been removed as it was not sufficiently sensitive to measure the small mass changes due to the oxidation reactions.

Experiments are made with both dried and undried 100 g samples of freshly ground coals; the particle size is either 50 to 70 mesh or 100 to 200 mesh. The sample is placed in the calorimeter and brought to the test temperature (set point) in a stream of flowing nitrogen, at which time the sample and oven (inner) temperatures agree to within 0.1°C. The calorimeter is put into an automatic control mode and the sample exposed to a flowing stream of dry or moist air for a period of at least 24 hours, unless self-heating occurs earlier. An air flow rate of 50 cm^3/min has been found optimum for self-heating in this apparatus. The sample temperature is varied to define the minimum temperature for self-heating, as evidenced by a significant temperature rise of the

sample. In these determinations, the automatic temperature controls must be carefully adjusted to ensure that the observed temperature rise is not attributable to any 'boot strapping' effect by systematic deviations of the oven temperature controls. Thus, it is important that the sample oven temperature does not exceed the sample temperature during any self-heating.

A sketch of the British Coal adiabatic apparatus (Lee and Wardropper, 1976) is reproduced as Figure 3-4. There is a tubular glass vacuum jacketed reaction vessel which contains approximately 15 g of coal sample. It is immersed in a 4 L Dewar flask containing water. Reactant gas is pre-heated to the coal temperature and enters the reaction vessel through the inlet in the base. A rise in coal temperature is sensed by a platinum resistance thermometer, and an electronic control unit maintains the coal and water temperatures to within 0.01°C. Two humidifying bubblers may be used if desired; one is immersed in the Dewar and saturates the inlet gas at the temperature of the coal. Alternatively, the exterior bubbler is water jacketed and may be operated at any fixed temperature. Platinum resistance thermometers in the coal sample and water bath are connected to electronic circuitry which controls the water heater so that temperature balance is maintained and heat flow is prevented.

The effluent gas from the reaction vessel is dried and analysed by a UNOR for CO and a Servomex for oxygen.

The 15 g sample is sized to below 0.2 mm (72 BS sieve) and put in the reaction vessel. Storage is in nitrogen wherever possible. Nitrogen is passed through the sample for two days at 30 mL/min to dry the coal, and the water bath temperature adjusted to the desired starting

temperature (usually 70°C). Air then replaces the nitrogen and the oxidation reaction commences.

The method has a number of shortcomings, with results not repeatable and the necessity to initiate tests above 50°C - 70°C. There are relatively large heat losses from the apparatus. Improvements suggested by the designers include: larger sample, sample preparation totally in nitrogen; more insulation and improved gas flow.

The Japanese researchers Onitsuka and Watanabe reported in 1982 on **'The Spontaneous Heating Properties of Coals'**. They used an air-bath adiabatic calorimeter as shown in Figure 3-5.

ASTM E771-81 is a standard test method for **'Spontaneous Heating Tendency of Materials'**. A sketch of the apparatus used is reproduced in Figure 3-6, and is an example of using an oil bath around the sample well. The apparatus has been classed as adiabatic since the oil bath is heated to maintain its temperature to within 2° - 3°C below the sample temperature provided the hot-plate output is sufficient.

Heated air is passed through a 15 g sample of coal at greater than 0.8 L/min. Sample temperatures are measured and time-temperature curve plotted to extrapolate to the minimum bath temperature at which spontaneous heating can be expected.

Tests are repeated at different initial bath temperatures and different sample conditions.

The test is considered elementary when applied to coal and should only be used to give a broad indication of relative susceptibility to spontaneous combustion.

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J.A. Shonhardt (Coal Jnl. Nov.1984), University of New South Wales, Australia, designed an adiabatic calorimeter with a metal block as the surrounding media, as shown in Figure 3-7, and described in Appendix B. The advantages claimed include: metal heat sink can be specified in terms of dimensions and heat conductivity that other workers can duplicate; temperature fluctuations are minimised by the large metal sink; freedom of choice of thermal cycle; and it is possible to supply sufficient heat to maintain adiabatic conditions when the coal temperature is rapidly increasing. There has to be a balance between the need to increase thermal capacity to eliminate temperature fluctuations and to have a responsive system to follow temperature changes in the sample. The test procedure involves heating a 25 g sample of coal to a predetermined temperature in a nitrogen atmosphere, then incubating it in oxygen and observing its self-heating behaviour while maintaining adiabatic conditions. The oxygen atmosphere may be humidified or dry and the sample may be moist or dry. The temperature time curve and heat of reaction calculated are related to susceptibility.

In the Adiabatic Storage Test (AST) used by Heemskerk (1984) the heat generated at nearly adiabatic conditions by reacting or decomposing substances is determined as a function of time. The AST is applicable to solids, liquids, pastes and dispersions.

The AST shown in Figure 3-8 consists of a 1.5 L Dewar vessel sealed with a stainless steel lid. This lid is provided with insulating material on the inside. The Dewar vessel is placed in an oven. The temperature of the oven is kept equal to the temperature of the sample in the Dewar vessel. In this way the heat loss is kept at a minimum and a nearly adiabatic condition is created.

An internal electric heating coil is used to heat the sample to the desired initial temperature. The heating coil is also used to determine the specific heat of the sample.

A gas can be led through the Dewar vessel by means of tubes passing through the lid of the vessel. From the inlet tube the gas is spread over the bottom of the Dewar vessel. The gas outlet is at the top of the Dewar vessel. Thus the entire sample is brought into contact with the gas. Before being supplied to the Dewar vessel the gas is carefully thermostated at a temperature equal to that of the sample. Because of the nearly adiabatic conditions (the maximum heat loss is 10 mW) the heat generated by the sample is almost completely converted into an increase in temperature of the sample. Therefore, the temperature of the sample is recorded continuously as a function of time. From the increase in temperature in relation to the specific heat and the mass of the sample the heat generated by the sample can be determined.

An experiment is discontinued when the heating rate is too fast. In this case the system is cooled down with the aid of a cooling coil. Measurements can be performed in the temperature range from -20°C to 200°C.

Even at relatively low temperatures small heat generations can be determined. The smallest temperature increase that can be determined corresponds to a heat generation of 15 mW/kg. The upper limit is determined by the capacity of the cooling coil. If water is applied as coolant a maximum heat generation of 500 W is allowed. The accuracy of the measurements is at least 30% at 15 mW/kg and 10% from 100 mW/kg to 10 W/kg.

3.5 PACED ADIABATIC NON-ISOTHERMAL CRITERION

In order to overcome the time factor inherent in the adiabatic method, the paced adiabatic non-isothermal criterion (PANIC) was introduced by British Coal in 1970. This consists essentially of passing a stream of air or oxygen, nitrogen, etc., through a bed of coal in a tube placed in a reaction chamber (see Figure 3-9), which can be raised in temperature steadily, normally 35°C per hour. The exit gases are analysed continuously in a train of equipment consisting of both chromotographic and infra-red instruments. To distinguish between gaseous oxidation products and desorbed or distillation products, two experiments are carried out on each coal, one passing air and the other passing nitrogen through the coal bed. The difference between the concentration of a gas at any temperature is due to oxidation.

A comparison between the results of adiabatic tests and those obtained from the paced adiabatic non-isothermal method, which enables a test to be completed in a day, has shown that there are no fundamental differences in the conclusions, either regarding the liability to spontaneous combustion or the temperature sequence pattern in which gases arising directly from 'oxidation' occur.

Reactivity as measured by oxygen deficiency in the off-gases is plotted against temperature. The most reactive coals show a rapid increase at about 73°C whereas the least reactive anthracite had slow reaction rates up to 140°C.

Shonhardt (1984) uses his calorimeter in a similar manner, except that he injects heat at a constant rate. As a result of the calorimeter control system attempting to preserve adiabatic conditions, a linear

heating rate is imposed on the sample and any deviations from linearity are due solely to heat production from the coal itself.

3.6 IGNITION TEMPERATURES

The USBM adiabatic test described in paragraph 3.4 determines the minimum temperature for self-heating of a coal.

A number of other methods have been used to determine a so-called ignition temperature at which oxidation becomes rapid and/or self-sustaining.

In one method (Acherjee, 1971), a sample is slowly heated in a furnace or bath while oxygen or air is passed through the sample. The ignition point is determined as the minimum temperature at which inflammation of the coal occurs, and can vary from 150°C to 500°C, depending on conditions and rank. The time elapsed until ignition is an indication of oxidation rate. The coal which has the lowest ignition point and shortest time to ignition is the most liable to spontaneous combustion.

In the Initial Temperature Method, coal samples are subjected to a current of air in a constant temperature oven set at a particular temperature. For each coal, a number of experiments are performed at different initial temperatures to determine the lowest temperature above which accelerated increase in temperature due to spontaneous combustion cannot be prevented.

The 'Crossing Point Temperature' method developed in India, provides a relatively simple test which has been utilized by research groups in several countries. A powdered coal sample is gradually heated in a suitable bath while air or oxygen is passed through the sample. The

temperature at which the coal bed crosses the bath temperature is defined as the crossing point temperature.

The apparatus used by Nandy, et al (1972) mainly consisted of a double-walled reaction vessel in the form of a U-tube, the annular space in between having been evacuated to minimise the heat transfer. The vessel was placed in a glycerine bath heated with an immersion heater. To maintain uniform temperature, liquid was stirred by bubbling air through the bath. A voltage stabilizer was used for maintaining a steady current to the heater and the temperature rise was regulated manually with the help of an auto-transformer. 20 g of coal sample sized below 0.21 mm (72 BSS mesh) was taken between two glass wool packings inside the reaction vessel. Air flow at 80 mL/min was maintained throughout. Humidity of incoming air was controlled by passing it through two consecutive water bubblers. The temperature of the bath was raised at a rate of $0.5^{o}C$/min.

A typical crossing-point curve is shown in Figure 3-10. The crossing-point or relative ignition temperature can be used as a guide to susceptibility, with coals having low relative ignition temperature being most susceptible. However, since the spontaneous combustion tendency is also dependent on the rate of heat generation this factor should also be considered. Feng, Chakravorty, et al (1973) proposed an index as follows:

$$\text{Index} = \frac{\text{Average Heating Rate Between } 110^{0}C \text{ and } 220^{0}C}{\text{Relative Ignition Temperature}} \times 1000$$

The average heating rate between $110^{o}C$ and $220^{o}C$ was used as the heating rate in this range is little influenced by evaporation of moisture or emission of volatile matter from the coal. Coals with an index below 5 are considered low risk, 5 - 10 medium, and greater than 10 high risk in respect of spontaneous combustion.

The crossing-point temperature test conducted by ACIRL (Cudmore, 1983) uses an apparatus based on that described by Kreulen (1948) and Kirov (1954).

In the test, 5 mL of a freshly prepared sample of closely sized coal (0.6 to 0.3 mm) is poured into a small aluminium furnace (Figure 3-11) which is electrically heated and programmed to increase in temperature at a rate of 2°C per min. Thermocouples are placed in the coal and in the aluminium furnace and carbon dioxide is passed through the coal at a rate of 50 mL per min until the temperature of the furnace and the coal becomes constant at 120°C. Oxygen at the rate of 200 mL per min. is then substituted for the carbon dioxide and there is a resultant rise in temperature of the coal caused by the exothermic heat of oxidation. The temperature at which the coal curve "crosses" the furnace curve is taken as the "crossing point" or relative ignition temperature. Duplicate tests are conducted and repeatability is $\pm$2°C. Regular tests are conducted on reference "safe" and "troublesome" coals - anthracite and brown coal respectively and results for such coals are reported together with results for coal sample(s) under test. This permits comparison between different coals, and enables them to be "ranked" within limits.

At CANMET, Alberta (Chakravorty, 1986) the crossing point temperature determination is carried out using the experimental set up shown in Figure 3-12. An oven is used where the temperature can be programmed and increased at a predetermined rates. Thermocouples monitor coal bed and oven temperatures.

Coal sample preparation is done following a procedures where atmospheric oxidation is reduced to a minimum. Fresh coal is put in a container at the mine site immediately following sampling and the air in the container replaced with argon to maintain an inert atmosphere.

The samples are sieved to 60-200 mesh in size and equilibriated at 60% relative humidty over a 48 hour period in an inert atmosphere. Saturated air is passed through the coal bed (50 g) at a rate of 80 mL per min. The temperature of the oven is increased at a rate of 0.5°C per min. The temperature of the oven and coal bed is monitored on a continuous basis during the experiment.

3.7 CHEMICAL METHODS

Chamberlain (US DOE ET-77-C-01-8965) described chemical methods of assessing the tendency of coals to spontaneous combustion as having the advantage that, if meaningful, they are very simple to carry out.

For example, it has been suggested that bromine absorption by coal could be used to measure in a few minutes its tendency to spontaneous combustion, since it has been shown that coal exposed to air for a few hours at 265°F absorbed much less bromine than unexposed coal. Other work has used iodine instead of bromine and concluded that iodine-absorption value was a measure of liability to spontaneous combustion.

Attempts have been made in the USSR and Poland to avoid some of the disadvantages of using gaseous oxygen by measuring the lowest temperature at which explosion will occur when the coal is intimately mixed with a solid oxidising agent such as sodium nitrite. Mixtures of 0.1 g of ground coal and about the same amount of sodium nitrite were heated in test tubes in a copper block, the temperature of which was raised at 4.5°C per minute. The 'ignition temperature' (slight explosion) of the sample was measured as received, after oxidation with hydrogen peroxide, and after admixture with benzidene to restore the sample to its condition prior to mining. It was concluded that the degree of reduction in 'ignition temperature' by treatment with hydrogen peroxide

was a measure of liability to spontaneous combustion. It was stated that the difference between the exploding temperature after treatment with H_2O_2 and after treatment with benzidene (ΔT) is an index of self-ignitability, and that if ΔT is below 30°C a coal is not liable to spontaneous combustion but above 40°C the coals are very liable. British Coal tested 30 coals with method (but substituting p-phenylene diamine for benzidene, which is a 'prohibited' chemical) giving ΔT varying from 15°C to 68°C.

R.N. Singh (Appendix C) describes further chemical methods as follows:

The change of 'permanganate number' during oxidation has been suggested as a measure of the degree of oxidation of coals. The number represents the cubic centimeters of (N) potassium permanganate solution reduced by 0.5 g (dry ash-free basis) pyridine-extracted coal in 1 hour at 100°C (Acherjee 1971).

The determination and measurement of the content of peroxygen bodies formed during the oxidation reaction was thought to be a useful measure to predict the extent of oxidation of coals (Chalishazar and Spooner 1956).

Hurby (Cerny et al 1970) determined the combustion point with an initial constant temperature of 165°C together with a flow of oxygen and expressed the 'relative oxidation degree' as follows:

$$0_S = \frac{T_2act - T_2ox}{T_2act} \times 100$$

where T_2act = the combustion point of coal in an active 1% aniline solution.

T_2ox = the combustion point of coal in a 1% oxident hydrogen peroxide solution.

Eastern European investigators have been more involved in chemical methods and since the 1960's their work has concentrated on the measurement of the decomposition of coal in hydrogen peroxide under adiabatic conditions (Lason 1959, Maciejasz 1959). The procedure used by Maciejasz is as follows:

A 3 g sample of coal, crushed to a size consisting of less than 0.06 mm was moistened with 1.5 ml of distilled water and placed in a Dewar flask which is standing in a bath heated to 18°C. When temperature parity is reached, 9 ml of 20% hydrogen peroxide was added. The hydrogen peroxide and coal was mixed, a thermometer was placed in the plug closing the vessel and the temperature was raised. At first, the time-temperature curves are virtually horizontal (Figure 3-13). The shorter the length of this section, the more reactive the coal tested.

Lately, this method had been used in France (Pregermain 1976) where coal samples were crushed in a nitrogen atmosphere to -0.063 mm size. The sample was then moistened with 5 ml distilled water and when it had cooled it was placed in the Dewar flask. 30 ml of 20% concentration hydrogen peroxide was added and the time-temperature variation recorded.

For practical purposes, the initial absolute temperature is taken to have no effect on the reaction. The time (t) taken for the temperature to increase by 65°C (dT) is measured (eg 90°C if the initial temperature is 25°C). The index I is then obtained by the following formula:

$$I = \frac{100}{t}$$

Where t is expressed in minutes. The shorter the reaction time, the higher the index. An I greater than 16 signifies potentially severe spontaneous combustion problems. However, results could be misleading due to catalytic decomposition of hydrogen peroxide resulting in heat evolution.

British Coal did some work on the examination under an infra-red microscope of a freshly-exposed coal section in an oxidising atmosphere. This is a method which did not destroy the physical structure of the coal as it examines the cut face of a lump. At first, small white spots are observed as oxidation proceeds, and these increase the area. It was thought possible to assess the rate of oxidation of a coal by counting the number of spots formed or the areas of white patches after a given time. No details are available of the results or development of this method.

3.8 LARGE SAMPLE TESTS

A number of researchers have tried to develop tests which involve use of large sized samples.

CERCHAR (Chauvin et al, 1986) use laboratory adiabatic test to determine reaction kinetics. The laboratory tests are made on samples of finely ground coal that has been homogenised and consequently, particle size effects and the heterogeneity of the coal's structure and composition are not taken into account. To overcome these problems, two tests were developed using samples of around 1 tonne in weight:

- A set of experimental hoppers from 3.5 m^3 to 5.5 m^3 in volume for finely ground coal in order to study the scaling effect of heat and mass transfer (Figure 3-14).

- A tank with controlled heat losses where air is blown through run-of-mine coal (Figure 3-15). The controlled air stream can be preheated up to 50°C and moistened to the desired level. The air exits the chamber by a tube in the lid and can be analysed. It is possible to operate the container in a near adiabatic mode.

It is claimed that the results from the controlled heat loss tank take into account factors such as particle size distribution, humidity and heterogeneity of the coal and are useful in predicting the risk of self ignition of run-of-mine or product coals in stockpile or during transport.

Van Doornum (Power and Plant, 1970) conducted experiments in South Africa using insulated test bunkers which held 10 tonnes of coal sample. Air was percolated through the coal and the temperature in the interior of the bunker measured by a number of resistance thermometers.

A coal with a susceptibility to spontaneous combustion would show a slow increase of temperature up to a maximum (5°C - 30°C above ambient) after 3 to 6 weeks and a slow decrease thereafter. For a reactive coal the temperature will increase rapidly and continuously without any sign of stabilizing.

For other coals the temperature rise may be very small but continuous, showing the coal could catch fire after a long period of time in a large stockpile that was not properly compacted and sealed.

Stott (1985) has also developed an apparatus using a large sample of coal. The 0.3 m diameter x 2 m long stainless steel cylinder is filled with approximately 90 kg of sample (crushed to below 2 mm) and air passed through. Fifteen separate electrical heaters wound directly onto the stainless steel control its temperature profile to match that of the coal. The heaters are controlled by signals from differential

thermocouples. One junction is in the centre of the cylinder surrounded by the coal sample and the other is cemented to the cylinder at the same level. Cooling coils are incorporated to ensure the temperature of one section of cylinder does not exceed that of the corresponding coal sample due to transfer of heat from an adjacent section. A sketch of the apparatus is provided as Figure 3-16.

The Prins Maurits Laboratory, the Netherlands, have used 10 tonne samples of coal with various degrees of compaction to validate their self-heating simultation model.

In Canada, large scale tests have involved stockpiles between 150t and 750t. Coal, dried to different moisture levels or treated with inhibitors, was laid down in piles to determine the time required to the onset of spontaneous combustion. It was found that inhibitors that were effective during laboratory testing, proved ineffective on a large scale due mainly to the creation of new oxidation surfaces exposed by degradation during handling.

3-9 DIFFERENTIAL THERMAL ANALYSIS (D.T.A.)

The technique consists of heating a small test specimen at a rate of 5°C/min and continuously recording the instantaneous temperature difference (dT) between it and a reference material (calcinated alumina) which is heated under almost identical conditions (Banerjee and Chakravorty, 1967; Berkowitz, 1957). The corresponding temperature of the inert reference material (T) is also noted in order to draw the resultant thermogram which is a record of (dT) versus (T) (Figure 3-17). The thermogram is explained in three stages. In the first, the temperature of coal decreases to a minimum (dT is negative) and then starts increasing which is defined to be the second stage. The third

stage shows very steep rises in heat evolution. The study of the second stage was thought helpful for the understanding of the self-heating characteristics of coal.

3-10 THERMAL GRAVIMETRIC ANALYSIS (T.G.A.)

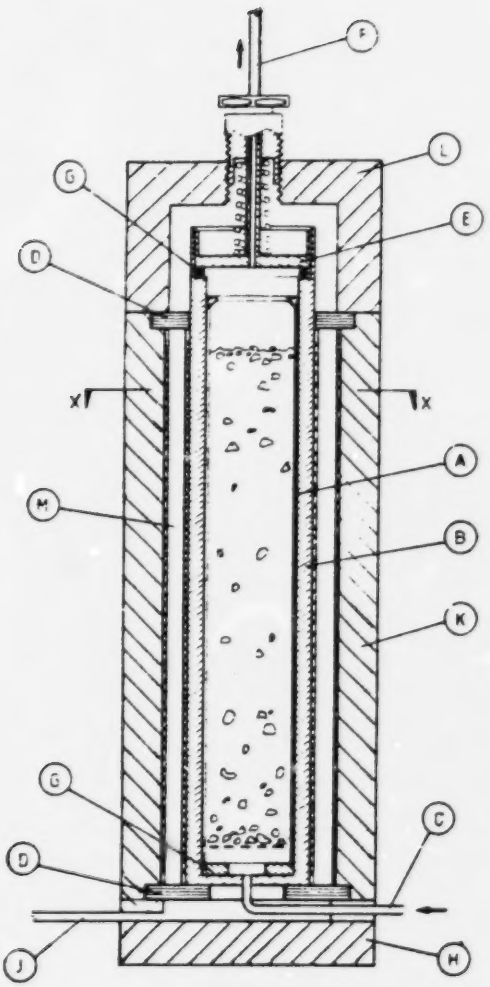
In this method the change in weight of the sample as it is heated in an oxidizing atmosphere is used as a measure of susceptibility to self-heating. Initially there is a decrease in weight as moisture is driven off, followed by a gain in weight as oxygen is adsorbed onto the coal. As temperatures rise the coal/oxygen complexes break down giving off more gases and the weight drops once more.

Cerchar, France, have experimented with a combined T.G.A./D.T.A. apparatus but have had difficulty obtaining reproducible results. Interpretation of the curbes is not considered easy.

FIGURE 3-1

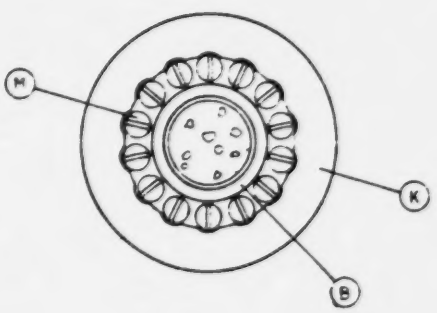
SPONTANEOUS COMBUSTION TEST APPARATUS

CALVET TYPE ISOTHERMAL CALORIMETER



LEGEND

A. removable brass tube
B. inner brass cylinder
C. gas inlet
D. reinforced fibreglass board
E. spring loaded plug
F. gas outlet
G. rubber washers
H. base
J. tube for electrical connections
K. main body
L. cap
M. thermopile

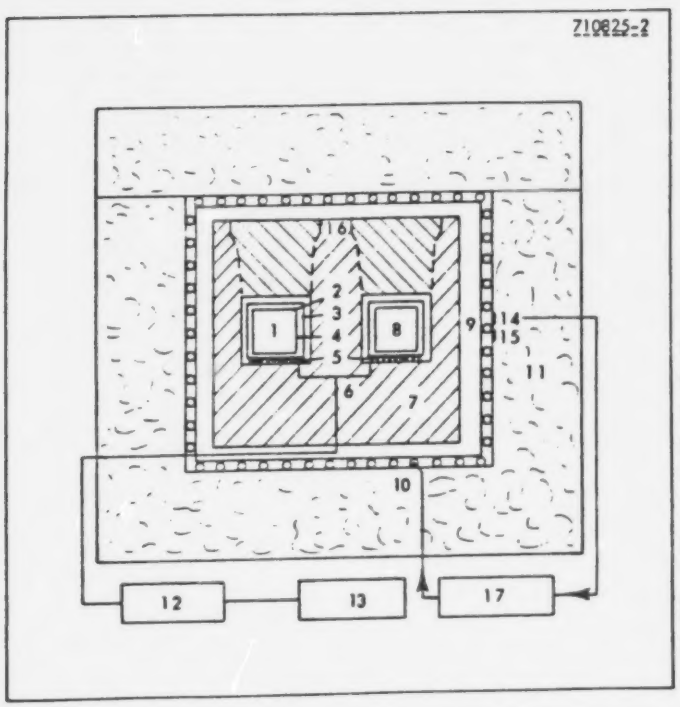


Source: Nordon et al, 1985

AR-112

FIGURE 3-2
SPONTANEOUS COMBUSTION TEST APPARATUS

ISOTHERMAL STORAGE TEST

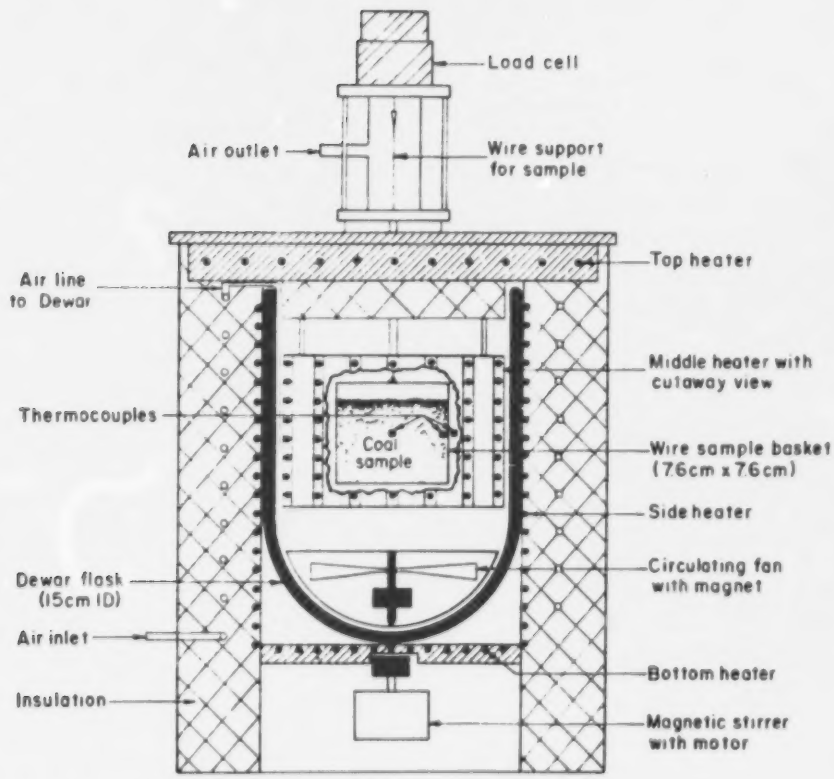


1 sample
2 sample vessel
3 cylindrical holder
4 air spaces
5 peltier elements
6 electric circuit
7 aluminium block
8 inert material
9 air space
10 heating wires
11 glass wool
12 amplifier
13 recorder
14 platinum resistance sensor for temperature control
15 platinum resistance sensor for safety control
16 platinum resistance thermometer
17 temperature controller

Source: Heemskerk, 1984

FIGURE 3-3
SPONTANEOUS COMBUSTION TEST APPARATUS

SCHEMATIC OF ADIABATIC HEATING APPARATUS

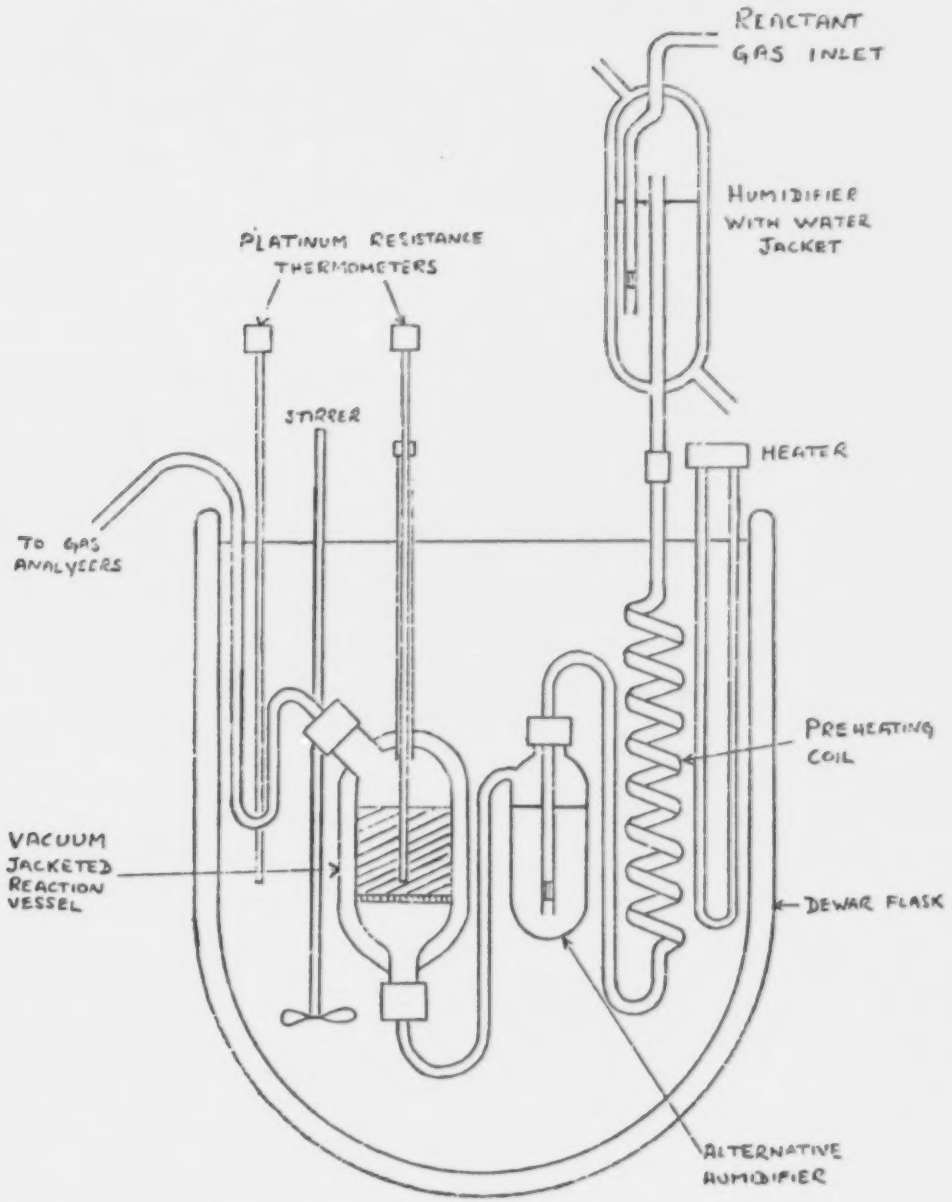


Source: USBM RI 8474

FIGURE 3-4

SPONTANEOUS COMBUSTION TEST APPARATUS

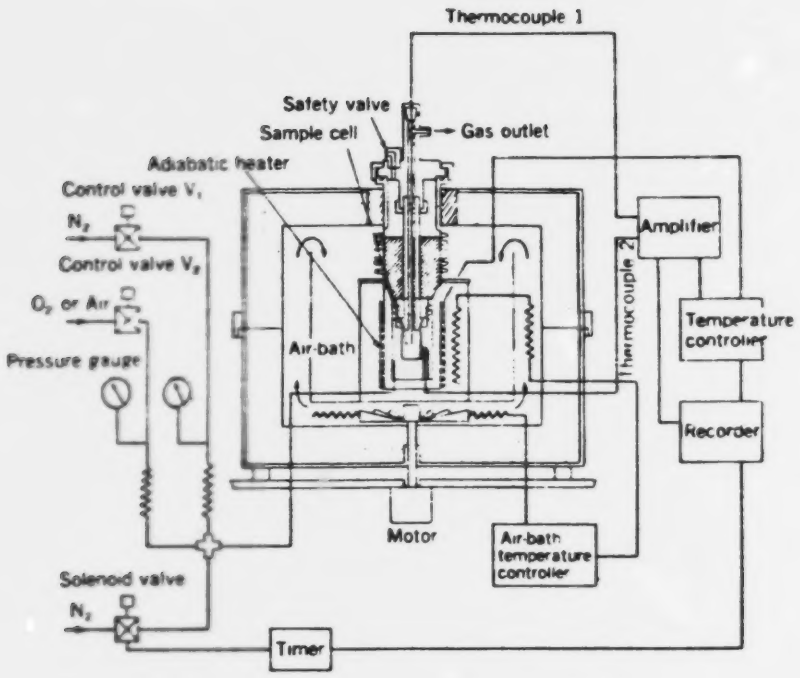
BRITISH COAL ADIABATIC APPARATUS SCHEMATIC



Source: Lee and Wardropper

FIGURE 3-5
SPONTANEOUS COMBUSTION TEST APPARATUS

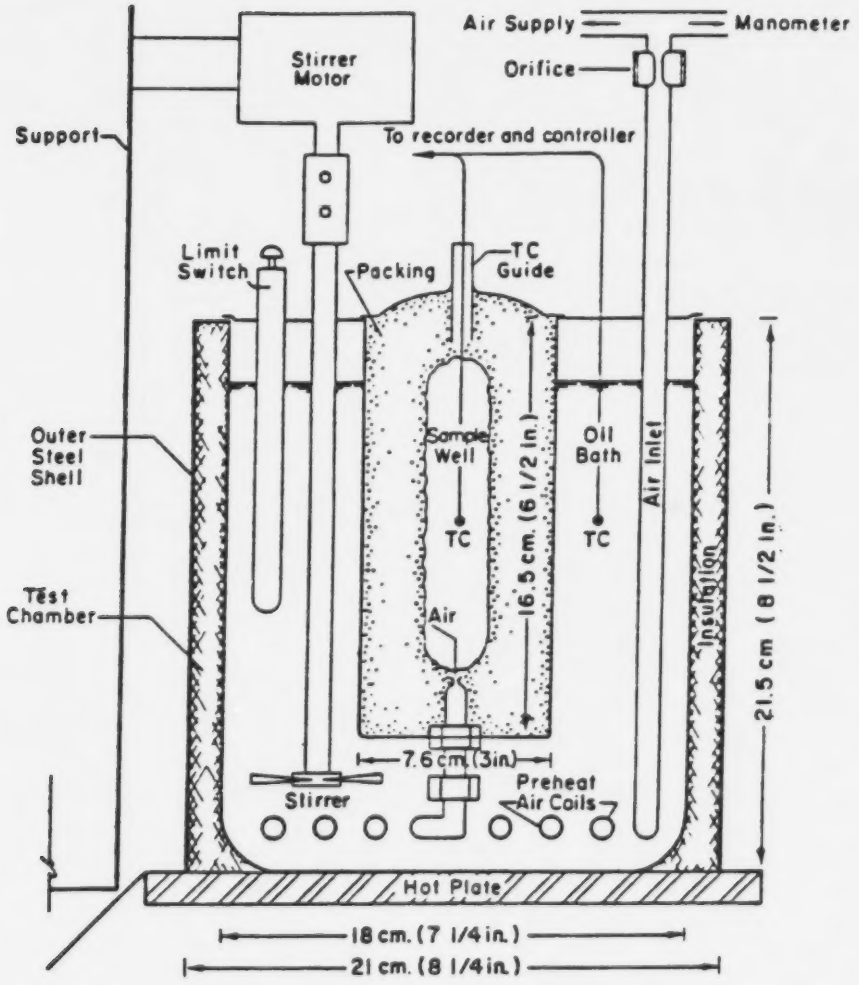
JAPANESE ADIABATIC APPARATUS



Source: Onitsuka and Watanabe, 1982

FIGURE 3-6
SPONTANEOUS COMBUSTION TEST APPARATUS

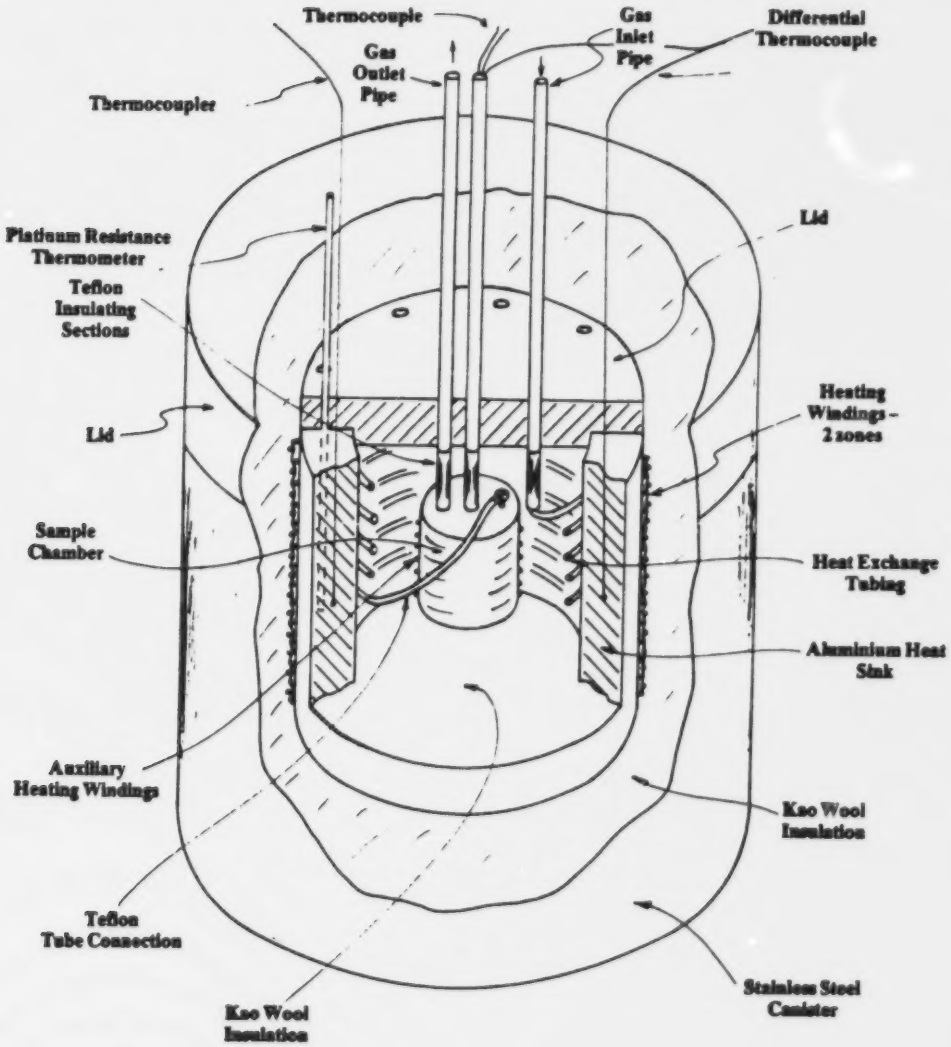
ASTM SPONTANEOUS HEATING APPARATUS



Source: ASTM E771-81

FIGURE 3-7
SPONTANEOUS COMBUSTION TEST APPARATUS

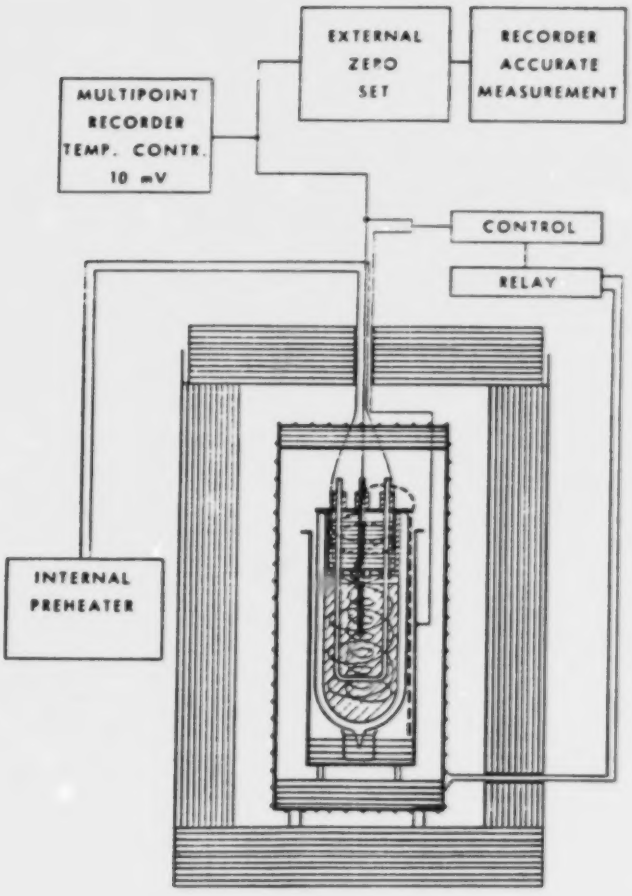
AUSTRALIAN ADIABATIC CALORIMETER



Source: Shondhart (Coal Jnl. 1984)

FIGURE 3-8
SPONTANEOUS COMBUSTION TEST APPARATUS

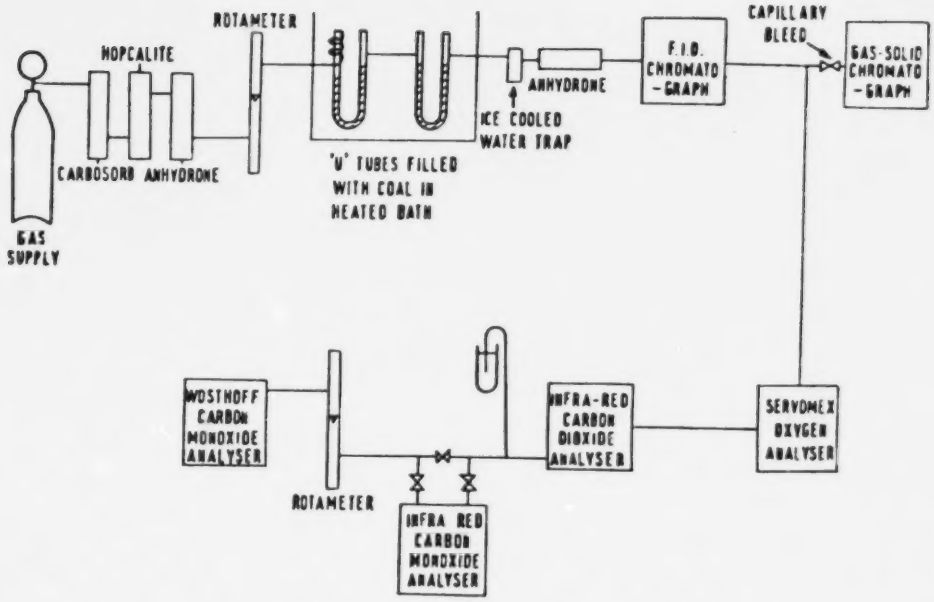
ADIABATIC STORAGE TEST



Source: Heemskerk, 1984

FIGURE 3-9
SPONTANEOUS COMBUSTION TEST APPARATUS

P.A.N.I.C. APPARATUS

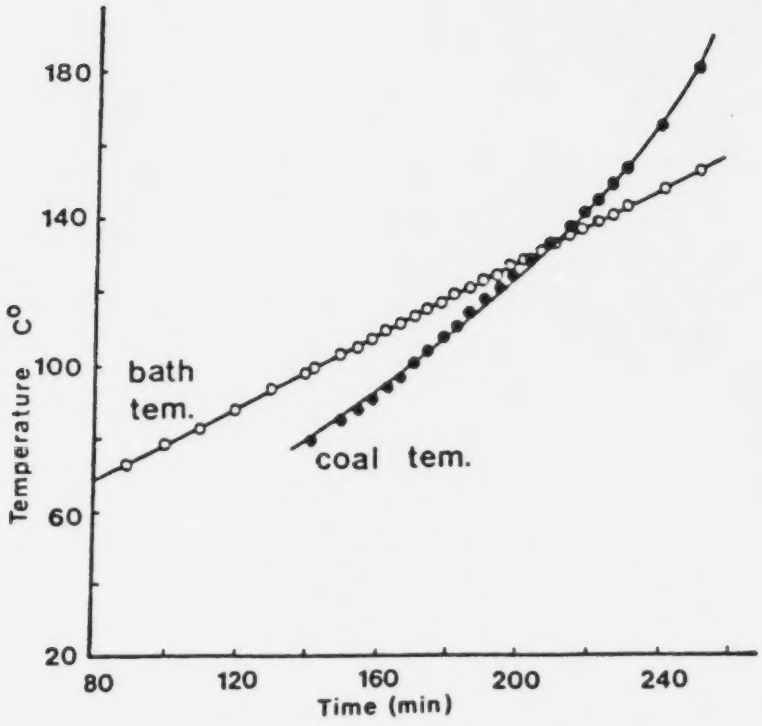


Source: Chamberlain (Mining Eng. 1970)

FIGURE 3-10

SPONTANEOUS COMBUSTION TEST APPARATUS

CROSSING-POINT TEMPERATURE METHOD

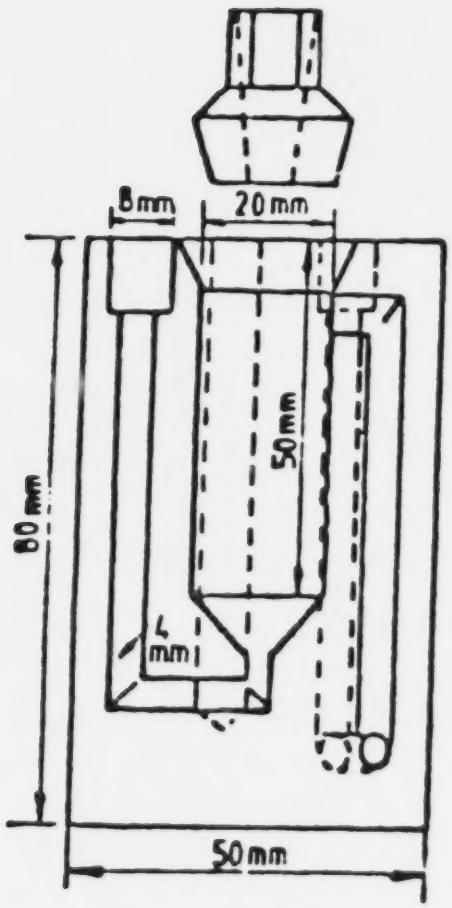


Source: After Banerjee et al 1972

FIGURE 3-11

SPONTANEOUS COMBUSTION TEST APPARATUS

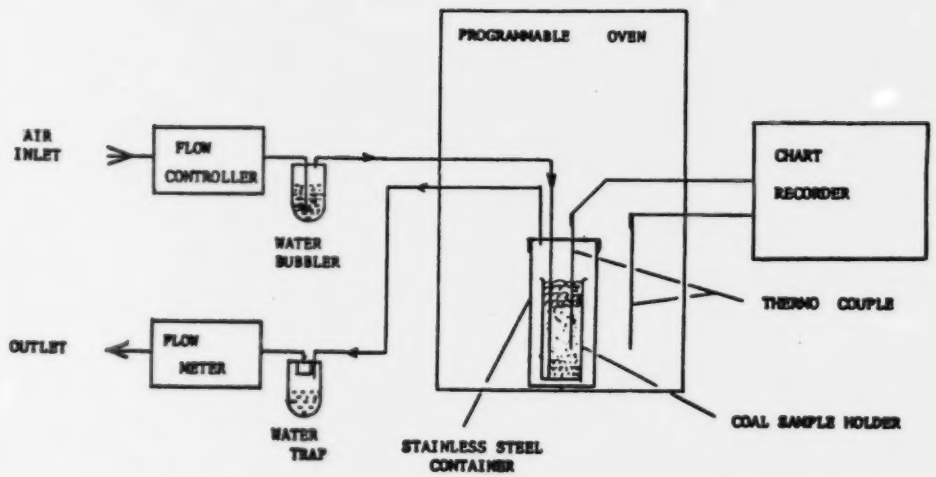
ALUMINIUM FURNACE FOR CROSSING-POINT DETERMINATION



Source: Cudmore (1983)

FIGURE 3-12
SPONTANEOUS COMBUSTION TEST APPARATUS

CROSSING POINT TEMPERATURE APPARATUS

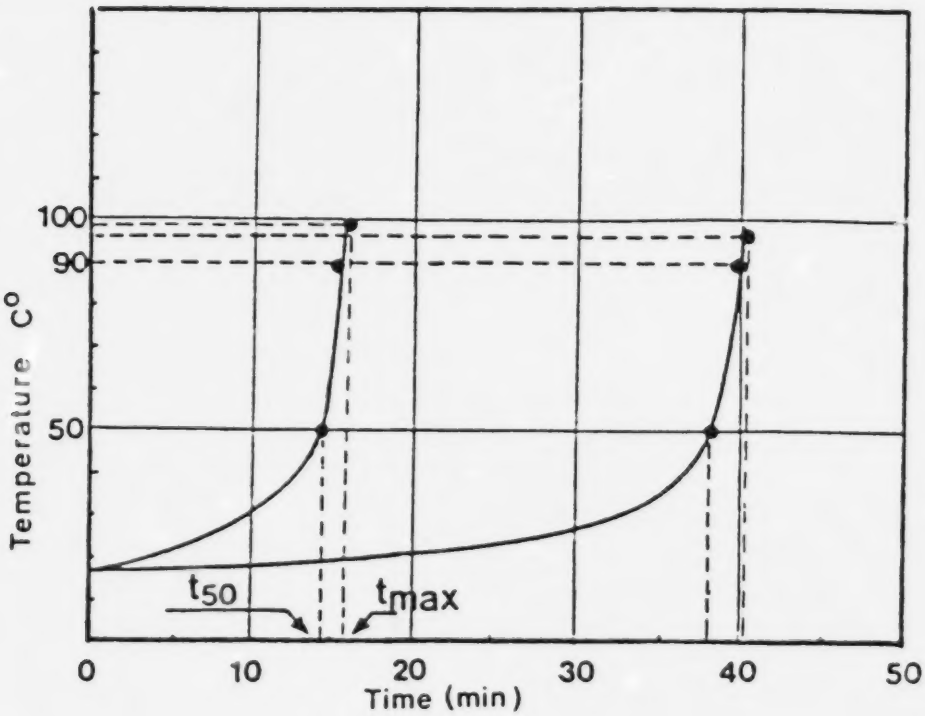


Source: Chakravorty (1986)

FIGURE 3-13

SPONTANEOUS COMBUSTION TEST APPARATUS

TYPICAL TIME TEMPERATURE CURVES

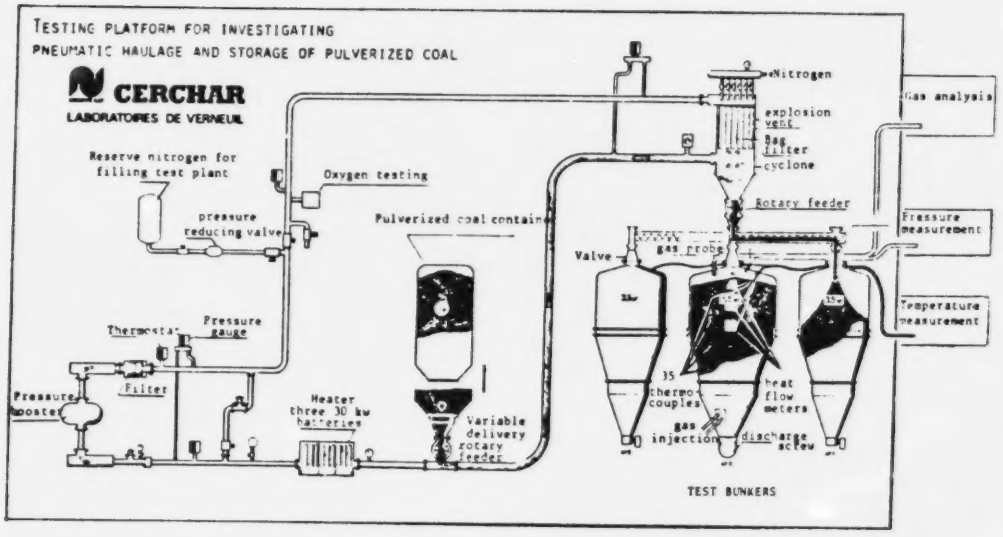


After Pregermain

AR-112

FIGURE 3-14
SPONTANEOUS COMBUSTION TEST APPARATUS

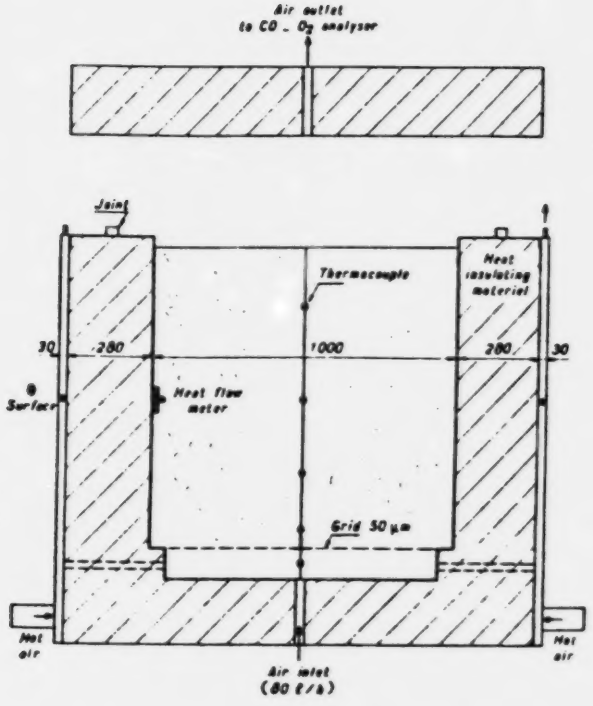
CERCHAR TEST BUNKERS



Source: Chauvin et al, 1986

FIGURE 3-15
SPONTANEOUS COMBUSTION TEST APPARATUS

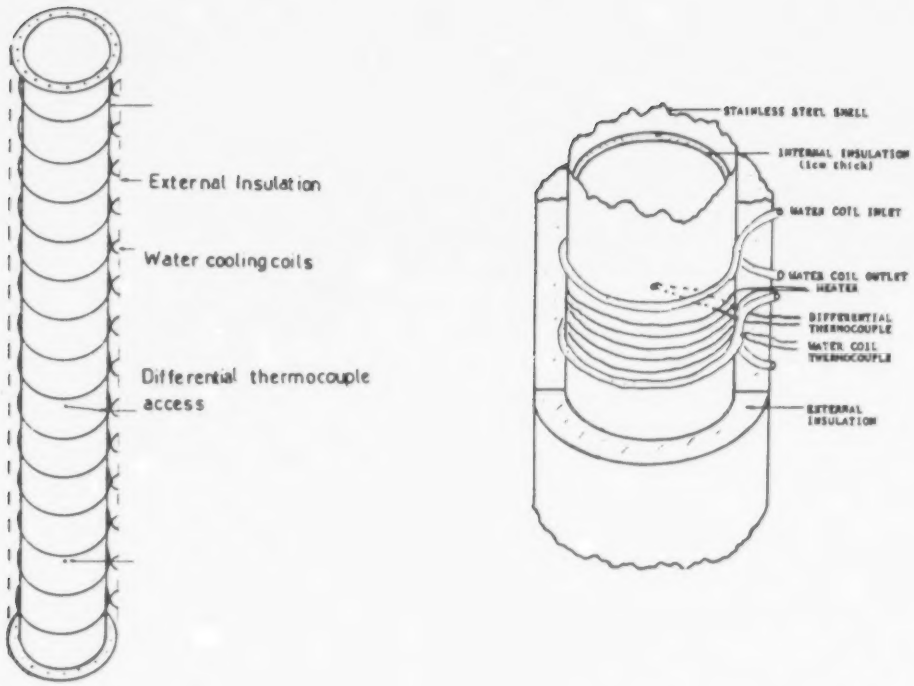
CONTROLLED HEAT-LOSS TANK



Source: Chauvin et al, 1986

FIGURE 3-16
SPONTANEOUS COMBUSTION TEST APPARATUS

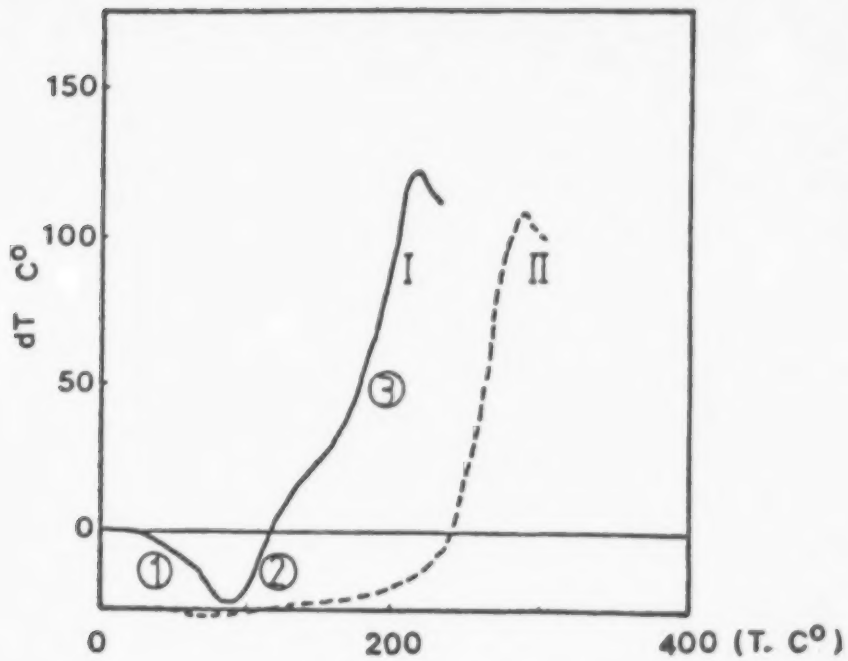
STOTT 2m TEST APPARATUS



Source: Stott, 1985

FIGURE 3-17
SPONTANEOUS COMBUSTION TEST APPARATUS

DTA THERMOGRAMS



I - Highly susceptible to heating
II - Not very susceptible to heating

Source: After Banerjee and Chakravorty, 1967

SPONTANEOUS COMBUSTION TEST APPARATUS
PHASE 1

SECTION 4 - CURRENT INTERNATIONAL PRACTICE

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FIGURES
(Following Text)

4-1 Self-Ignition Apparatus

4-2 Self-Ignition Test

4-3 Methods of Testing for Susceptibility to Spontaneous Combustion

CURRENT INTERNATIONAL PRACTICE

4.1 GENERAL

An important activity within this study was to determine current international practice, both in the research and operational environment. This section summarises the results of a survey using telephone, telex, letter and sub-contracted reports as means of communication. Where little response was obtained from these enquiries, the most recent published literature available has been consulted.

4.2 UNITED STATES

Most work is carried out at the Pittsburgh Research Centre of the US Bureau of Mines. They are investigating the kinetic parameters of the coal oxidation reaction and applying them to models of the self-heating process. An adiabatic calorimeter is used for the testwork which is similar to that described in the USBM RI 8474 (see paragraph 3.4). The humidity of the air is controlled into the apparatus and CO and O_2 measurements are recorded both in and out.

Attempts are made to relate oxidation parameters to petrographic composition, oxygen content and coal rank. For a new mine or seam the susceptibility to spontaneous combustion would be assessed primarily on the basis of oxygen content and rank with other testwork playing a secondary role.

A test used by a commercial laboratory is based on the procedure described by Shea and Hsu (1970). The apparatus (Figure 4-1) consists of a Dewar flask containing the coal sample and fitted with an oxygen inlet tube, outlet tube and a thermocouple well. During a test run, the

entire assembly is placed inside an oven at 74°C. The test is conducted by passing oxygen, saturated with water vapour when preheated to 74°C, through the sample. The temperature rise of the sample, due to heat exchange and oxidation is plotted against time and is an indication of the relative tendency of the coal to self-ignite. Plots are commenced at 38°C as shown in Figure 4-1, for three coals. Curve (A) is for a coal with little tendency to self-heat, curve (C) is for a very reactive coal, while curve (B) is for a coal that may self-heat if not handled with some care.

4.3 UNITED KINGDOM

A report by R.N. Singh on UK practice is included as Appendix C.

British Coal, the major coal operator in the UK, has a wealth of underground coal mining experience. All coal seams have been classified into various risk categories based on the incubation period method. The incubation period is defined as the time elapsed between the start of coal winning operations in a panel and the first sign of recognized heating. High risk coals have an incubation period of less than 3 months, while low risk coals have a period exceeding 18 months. When a coal mine is planned in a new seam, the physical, chemical properties and rank are determined in the laboratory and these are correlated with the spontaneous combustion risk potential.

British Coal's laboratories have facilities to carry out the Static Isothermal and the PANIC methods. The latter dynamic method was developed to investigate whether there was a better indication of spontaneous combustion than carbon monoxide and so is not commonly used to determine relative susceptibility.

Adiabatic test apparatus are available at various laboratories which evaluate coals liable to spontaneous combustion on behalf of major international coal mine developers and coal shipping companies.

An adiabatic apparatus is used for research at Nottingham University and is considered the best tool to assist in self-heating assessments.

4.4 THE NETHERLANDS

Extensive research has been carried out in recent years by Dr. Heemskerk and colleagues of the TNO Prins Maurits Laboratory, Chemical and Technological Research Institute in the Netherlands. They have investigated in particular the self-heating characteristics of sub-bituminous coals during storage. (Note: The coal tested would be classed as high volatile bituminous under the ASTM classification system).

An isothermal test was used for determining the relationship between temperature and heat generation of the coal sample under different conditions, such as oxygen concentration.

An adiabatic test apparatus has been used to determine the equilibrium point between moisture in the gas phase and in the solid phase, called the adiabatic saturation temperature. The effect of airflow rate on this parameter was studied.

The process of self-heating in stockpiles was modelled with particular reference to ventilation conditions and coal reactivity. The model was evaluated by large scale storage tests (10 tonne samples) over a period of time. Work continues to refine the model which can pin-point with some accuracy the location where heatings can be expected in piles of various compactions.

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Thus both isothermal and adiabatic tests are thought appropriate in the study of self-heating in stockpiled coal.

A report on a vist to PML is included in Appendix E.

4.5 AUSTRALIA

While the general incidence of spontaneous combustion in Australia is reported to be quite low, it is known that in certain areas spontaneous combustion is a problem. Consequently there are a number of laboratories undertaking research and testing for susceptibility.

The Australian Coal Industry Research Laboratories (ACIRL) use the adiabatic method primarily, but do, on occasion, use the crossing-point temperature method.

Commonwealth Scientific and Industrial Research Organization (CISRO) have undertaken research and contract work on the subject for several years. Their experience is that because the spontaneous heating of coal depends on a large number of variables, no single laboratory test, with its quantitative ranking, is capable of providing all the necessary information to be of real assistance in the development of practical management strategies for the safe and efficient handling of coal prone to self-heating.

As a consequence, they make a suite of measurements of which oxygen absorption, heat of reaction, reaction kinetics are some. They note that because of the wide range of reactivity of coal to oxygen, the use of a standardized size and weight of sample is difficult.

Shondhart, at the University of New South Wales, has developed a calorimeter with metal heat sink that provides good temperature

control. The calorimeter may be operated as a purely adiabatic apparatus or in a ramping temperature mode for tests similar to the PANIC method.

4.6 INDIA

Much valuable research has been carried out by Indian researchers over the past 30 years. Work has included measuring the rate of peroxy-complex formation and the determination of oxidation rates and reaction rate parameters. However, mostly they have concentrated on more practical tests for assessing susceptibility favouring the crossing point temperature method, the differential thermal analysis method and ignition temperature methods. The results are combined with an assessment of extrinsic factors to produce a risk index. Banerjee S.C. (1985) describes test procedures in his book "Spontaneous Combustion of Coal and Mine Fires." His classification of testing methods is shown diagramatically in Figure 4-3.

4.7 NEW ZEALAND

J.B. Stott, University of Canterbury, New Zealand, has researched coal oxidation for over 30 years with particular reference to the influence of moisture. He has used differential thermal analysis and more recently, isothermal micro-calorimetry techniques to determine low temperature heats of reaction. He has designed a large sample device (90 kg sample) to measure temperature profiles when air is passed through coal. This apparatus acts basically in an adiabatic mode.

4.8 JAPAN

Japan has carried out fundamental work in the reaction kinetics of coal oxidation and their relationship to various parameters such as oxygen

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content and pressure of the oxidizing atmosphere, particle size, moisture content, etc. They use adiabatic methods in general.

4.9 EASTERN EUROPE

A report commissioned from KOPEX, Poland is reproduced as Appendix D and summarized as follows:

In eastern European countries different methods of testing coals for susceptibility to spontaneous combustion are used. Most tests utilize air as oxidizing agent although sometimes pure oxygen or an oxidizing chemical solution are used.

Oxidation effects measured include:

- increase in coal temperature
- consumption of oxygen or oxidizing agent
- emission of gassy products of reaction, especially carbon monoxide and dioxide
- production of non-gassy products of reaction such as humic acids or functional oxygen groups.

The methods used include isothermal, quasi adiabatic and paced adiabatic.

The criteria used for determining the susceptibility to spontaneous combustion include:

- quantity of oxygen consumed in specified time interval
- the rate of oxidation reaction
- ignition temperatures
- rate of temperature growth under specific conditions.

The best test method depends on the purpose of the test, since many factors affect the processes leading to self-heating. Quasi-adiabatic

tests most closely represent the actual conditions of self-heating at a laboratory scale, but isothermal tests can give valuable information on reaction kinetics.

For assessment of spontaneous combustion risk as opposed to detailed research other methods can be used.

Oplinski's method involves determining for an adiabatic point, the rate of increase in temperature of a 0.3 g coal pellet introduced in an air stream having a temperature of 237°C.

On the basis of this index, and taking into account the ash content of the coal sample tested, a classification system divides the coals into four groups of differing spontaneous combustion characteristics. The method is included in an industrial standard specification and has been widely applied in practice since the 1950's.

A research method developed in recent years determines the reaction rate of a prepared coal sample of 0.5 g mass treated with alkaline water solution of potassium permanganate at room temperature. The reaction rate is determined as the mean value for the first hour of oxidation. The results of these tests are correlated with test results obtained by Olpinski's method.

Ventilation engineers, when considering fire prevention, take into account tests for spontaneous combustion by Olpinski's method. The Olpinski's method has also been adapted for spontaneous combustion tests for coal in Czechoslovadia and Jugoslavia.

In the USSR there are two methods used: MakNII and IGD.

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In the MakNII method a 100 g coal sample of 0.3 - 0.43 mm grain size undergoes heating in an air stream at a rate of 25 K/min and for defined temperature intervals (150° - 200°C or 135° - 175°C) an index is determined which takes into consideration the mass of oxygen consumed and gas components produced (CO_2 and CO).

In the IGD method a 100 g coal sample of 1 - 3 mm grain size undergoes oxidation with air in a closed tank from which, at certain time intervals, air samples are taken for analysis and the negative pressure produced is eliminated by letting some fresh air in. The oxidation process runs at a temperature of 25°C. On the basis of test results one determines the mean value of a constant reaction rate determined for the time intervals of 50 - 250 h.

Over a long time span, Olpinski's method has proved successful in Poland in determining fire hazard risks and for determining guidelines for fire prevention during mining, storage and transportation of coal.

4.10 FRANCE

French research workers predominately from Cerchar have investigated spontaneous combustion for many years, primarily to reduce the number and severity of fires and heatings in their mines.

The adiabatic calorimeter was designed to investigate the influence of moisture on spontaneous heating of coal. It is considered important to isolate the effects of moisture from those of coal-oxygen reactions.

Pyrite, especially if finely divided, is considered to be responsible for initiating heatings in certain coals. The reaction with hydrogen peroxide is used as a quick method to detect pyrite.

D.T.A./T.G.A. studies were designed to compare coal reactivities in dry air, but results are considered inconclusive to date.

A more detailed report on Cerchar work is provided as Appendix E.

Large-scale tests involving storage of pulverized coal 3.5 m^3 hoppers are used to confirm mathematical models and scale-up from laboratory tests. In this case, isothermal tests on samples of different dimensions we used to obtain the scale up data.

4.11 CANADA

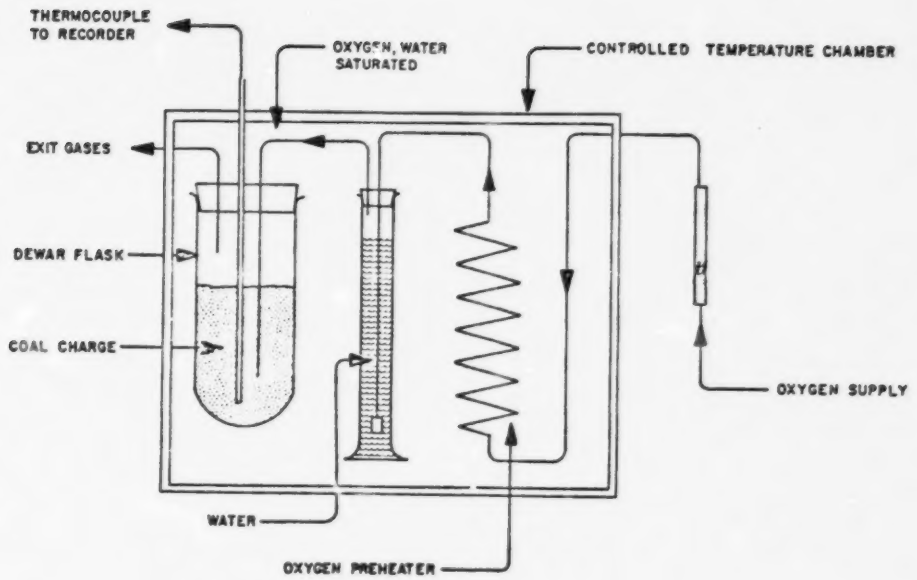
Canada has undertaken research on spontaneous combustion susceptibility for many years. Two types of problems have occurred. The first relates to heatings and fires in the underground mines of southeast British Columbia where the coals are low to medium volatile bituminous, ranks not normally susceptible. It is thought the mining method and geologic factors create conditions extremely favourable for self-heating. The second problem relates to the high-volatile bituminous coals which have to be partially dried to meet export market specifications. Severe spontaneous combustion problems have been encountered.

At the Coal Research Laboratory, CANMET, the test procedures used are primarily the crossing point temperature method (Figure 3-12) and oxygen absorption at isothermal conditions. In the latter method, 100 g of coal sample were placed in a 2 L enclosed container and the drop in pressure noted with time. The head gas was analyzed after 96 hours for oxygen and carbon monoxide using a gas chromatograph. The nature and extent of pressure drop was found to be useful in the categorization of coal for spontaneous combustion liability. CANMET also confirmed that there was a direct relationship between the exinite content of coals and their susceptibility.

Bachelor and Majumdar (1986) recently completed a study of the characteristics of 11 western Canadian coals. They treated coal samples with air or nitrogen of different relative humidities in an adiabatic apparatus to obtain data on susceptibility in the form of a temperature rise. The temperature rise was found to be related to equilibrium moisture content of the coal, residual moisture content after partial drying and the relative humidity of the flowing media. Qualitative data on the chemical structure of the coals was obtained using Diffuse Reflectance Infrared Fourier Transform analysis. Peroxygen contents were determined and related to other characteristics. The coals were examined for free radical content by Electron Paramagnetic Resonance, and the results were encouraging enough to justify further research.

FIGURE 4-1
SPONTANEOUS COMBUSTION TEST APPARATUS

SELF-IGNITION APPARATUS

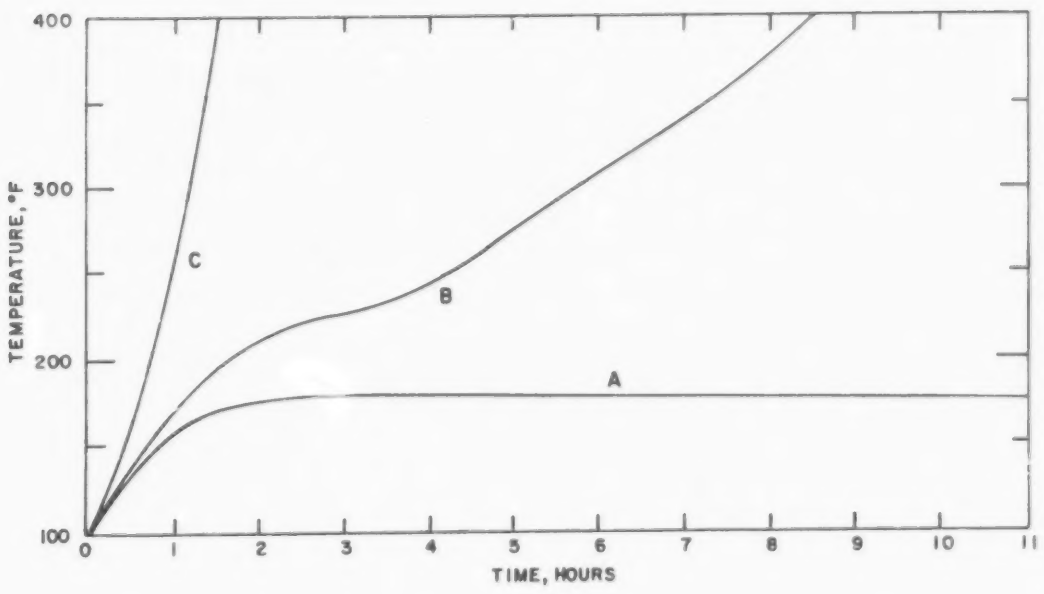


Source: Hazen.

FIGURE 4-2

SPONTANEOUS COMBUSTION TEST APPARATUS

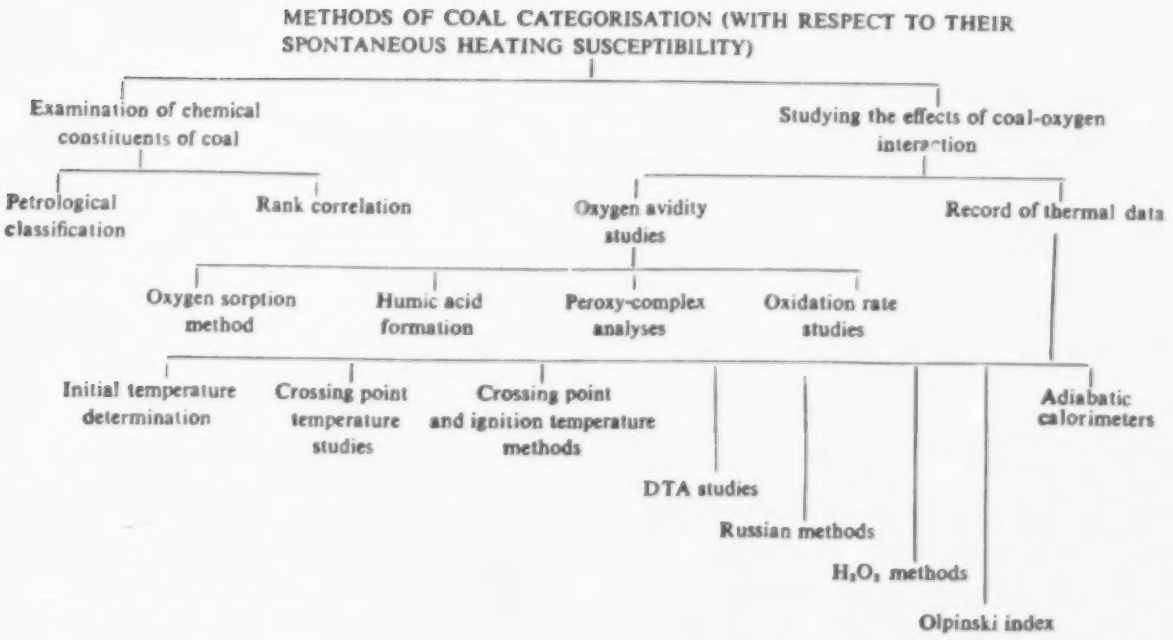
SELF-IGNITION TEST



Source: Hazen.

FIGURE 4-3
SPONTANEOUS COMBUSTION TEST APPARATUS

METHODS OF TESTING FOR SUSCEPTIBILITY TO SPONTANEOUS COMBUSTION



Source: Banerjee S.C. (1985)

SPONTANEOUS COMBUSTION TEST APPARATUS
PHASE I

SECTION 5 - COMPARISON OF TEST METHODS

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COMPARISON OF TEST METHODS

5.1 GENERAL

Comparison of the many different test methods for assessing the liability of a coal to spontaneous combustion depends upon the information required since each test is suited to study a particular aspect of the process.

CANMET requirements can be summarized as:

- Prime purpose is to provide the Canadian coal mining industry with a rapid assessment of the hazard of a particular coal for both underground and open-pit mines.
- To provide industry with an assessment of coal product characteristics during storage and handling and to indicate the effect of changes in product specifications (e.g., total moisture content) on these characteristics.
- To have a multi-sample apparatus so that a number of tests can be undertaken in a short time span.
- To be suitable for the small samples available from drill cores, i.e., 100 g sample, maximum.

The discussion of the merits of each of the methodologies relates to the above requirements.

5.2 STATIC ISOTHERMAL/OXYGEN ABSORPTION METHODS

These two methods are basically the same, though it can be argued that where a temperature differential is measured between the sample and surrounding atmosphere, the term iso-thermal should not apply.

Isothermal techniques are used to study the effects of coal parameters such as particle size, temperature, oxygen partial pressure, moisture, on the rate of oxidation at selected temperatures.

Advantages

- Techniques widely used so good base for comparison.
- Reasonable reproducibility between laboratories.
- Can obtain meaningful results at the low temperatures actually encountered during mining and processing operations.
- Small samples required.
- Multi-sample apparatus feasible since all samples would be under same temperature regime.
- Good for reaction heat determination.
- Low temperatures used do not drive off any chemicals used as surfactants.

Disadvantages

- Tests can take a long time. In standard oxygen absorption test, 96 hours is required. Other tests can take much longer particularly for coal with low susceptibility.

- In a closed system test, there is a pressure drop as oxygen is absorbed. The rate of oxidation is related to the partial pressure of oxygen in the surrounding atmosphere so this test does not fully reflect actual conditions in mining operations. The constant pressure method overcomes this problem.

- Absorption rates can depend on degree of pulverization and the amount of methane desorbed.

- The coal sample history has a considerable influence on the result of the test.

- Difficult to identify the effect of moisture.

5.3 ADIABATIC METHODS

Advantages

- Simulates conditions closely resembling the mine environment or stockpiles where spontaneous combustion may occur. Thermal conductivities in a large mass of coal are very poor and therefore adiabatic methods in which heat transfer to or from coal under test is virtually eliminated represents realistic test conditions.

- Useful for investigating self-heating rate of coal as opposed to heat production by isothermal methods, rank, petrography, chemical composition and of inhibitors.

- Used for study of gaseous products of oxidation over an extended range of temperatures.

- Changes in temperature can be measured accurately since there is no heat loss to the surroundings.

Disadvantages

- Cannot be multi-sample within one apparatus since temperature of the surroundings must be controlled to that of individual samples. Therefore, can only have multi-apparatus system with some common features.

- Gas measurements from multi-samples difficult.

- Experiments can take weeks or months to complete if started at ambient temperatures. Tests started at higher temperatures (70°C to 100°C) can take 1 to 5 days with some coals.

- By starting experiments at high temperatures (above 70°C), the critical temperature range of the initiation of spontaneous heating, where the reactions are different from normal chemical oxidation, is not investigated.

5.4 PACED ADIABATIC NON-ISOTHERMAL CRITERION

Advantages

- Speeds up adiabatic tests while classifying coals in same order of susceptibility as normal adiabatic tests.

- Useful in study of the gases arising from oxidation and their temperature sequence pattern.

- Since reaction chamber is raised at constant rate, several samples could be contained within the same controlled temperature environment.

Disadvantages

- Method not widely used for routine tests so no comparison of results possible.
- Extremely difficult to make multi-sample because essentially based on gas measurements.
- Does not provide absolute measurements on heat production.

5.5 IGNITION TEMPERATURES

This group covers ignition temperatures, initial temperature and crossing point methods.

Advantages

- Easily determined.
- Variables readily controlled.
- Widely used in various countries around the world.
- Readily adaptable to multi-sample aparatus.
- Limited measurements required.

Disadvantages

- Utilizes temperatures which are far above the temperatures encountered in coal mining environments.
- Results difficult to correlate to actual occurences in practice.

- Conditions of experiment such as rate of flow of oxygen/air, particle size of coal have to be meticulously maintained.

- Changes to standardised test conditions can introduce major differences in the crossing-point determination.

- There is an inevitable temperature lag between the sample and the bath during programmed heating which distorts any results.

- Method is relatively time consuming.

- Coals with high moisture can give misleading information, and moisture and oxygen effects overlap.

5.6 CHEMICAL METHODS

Chemical methods are generally based on the measurement of the rate of oxidation or changes in the chemical constitution of coal or by investigating the hydro-aromatic structure of coal.

Advantages

- Simple to carry out.

- Fast; can be completed within a few minutes.

Disadvantages

- No definite relationship found between results and susceptibility to spontaneous combustion.

- Need specialized knowledge of coal structures or coal reaction chemistry.

- Results can be misleading. For instance, in the hydrogen peroxide method, the catalystic decomposition of hydrogen peroxide may result in heat evolution.

5.7 LARGE SAMPLE TESTS

These tests can be extremely useful in determining the susceptibility of coals to spontaneous combustion since the physical nature of the sample need not be changed by crushing, etc. This is of particular importance when studying the effects of inhibitors applied to the coal surface or tests on pelletised or briquetted products, etc. However, because a large quantity of sample is used (up to 10 tonnes) then these methods cannot be applied using laboratory multi-sample apparatus or used on samples from drill cores. Consequently, they have been eliminated from further consideration.

5.8 DIFFERENTIAL THERMAL ANALYSIS

Advantages

- Uses small amount of sample (less than 1 g).
- The temperature history depicted by thermograms indicate the physical and chemical changes that occur at different temperatures.

Disadvantages

- Not quantitative, gives inconsistent and anomalous results.
- Essential to have standardized conditions if results are to be comparable.

- Requires almost identical geometrical spacing of the inert and sample holes relative to the furnace.

- Inert must have same packing density and mass as sample.

- The moisture diffusion rate through the sample, which is dependent on size distribution and packing density, affects the thermogram.

- Interpretation of results of thermogram can be subjective and therefore open to errors.

- Coal must be crushed to below 72 mesh.

5.9 GRAVIMETRIC ANALYSIS

Advantages

- Gives history of weight changes showing removal of moisture followed by oxygen absorption.

Disadvantages

- Results not reproducible and are inconclusive with current test procedures.

- Difficult to apply to multi-sample machine since each sample would need its own weigh-scale.

- Limited data available for comparison purposes.

5.10 MULTI-SAMPLE APPARATUS

The terms of reference call for a multi-sample apparatus. In doing so, there are a number of advantages and disadvantages:

Advantages

- A number of tests can be carried out simultaneously reducing the time period for any defined experimental program.

- Tests on samples are carried out under identical (or near identical) conditions and therefore can be directly compared. This factor is particularly important when considering the more empirical tests.

Disadvantages

- The adiabotic and thermal gravimetric tests are eliminated from consideration.

- The complexity that could arise in the manufacture of a multi-sample apparatus may lead to differences in detail that affect test results.

- Cost is higher than for a single sample apparatus of the same test.

The Bothermal test apparatus developed at the PML, Netherlands (see Appendix E) is an example of an apparatus which has been adapted to multi-sample operation. The tests involves no gas flows or programmed heating so adaption from the multi-sample apparatus are reproducible. Problems can arise while trying to duplicate other test procedures.

5.11 CONCLUSIONS

A number of laboratory methods for listing coals in order of liability to spontaneous combustion have been discussed. In all cases there is a relationship between rank and reactivity, but there are a number of anomalies indicating that although rank is an important factor, there are physical properties, e.g., porosity, associated with petrographic constituents which affect the oxidation of a coal. All the tests described except the large scale tests require a fundamental alteration in the physical condition of the coal, e.g., it has to be crushed and the various petrographic types become mixed. The tests, in general, confirm that oxygen content (which is closely related to rank) gives the best 'first' assessment of liability to spontaneous combustion, but this is affected at temperatures up to about 30°C by a number of secondary factors (e.g., oxidation of pyrites and chemisorption of moisture, etc.) which are additive and so complicate the process.

It would be of great value if there could be an agreed international method for laboratory testing to assess the liability of a coal to spontaneous combustion. Because of the need for a comparatively simple test, this would preferably be a standardized isothermal method or a method involving controlled heating which can reduce the time required.

For practical purposes related to underground mine monitoring, it is important to carry out programmed heating oxidation tests, particularly with any different types of coal to confirm that the order of appearance and the rate of evolution of detector gases, e.g., carbon monoxide, hydrogen, ethane, etc. are following the expected pattern.

The effect of coal processing procedures and use of inhibitors on a product's susceptibility to spontaneous combustion may need a modified test procedure since crushing the sample may fundamentally alter a treated coal's susceptibility.

The requirement of a multi-sample apparatus precludes the use of adiabatic methods as these would have to be multi-apparatus with some common features.

Chemical methods can be carried out quickly but are not suited to multi-sample automation and there is no general acceptance yet that the test results are good indicators of susceptibility.

Gravimetric methods are not widespread, and the high cost for a multi-sample apparatus using this method may not be justified.

The apparatus should be designed for one or more of the following types of tests:

- Isothermal
- Oxygen absorption
- Ignition temperatures
- Differential thermal analysis

A design which allows several different experimental procedures to be carried out has been recommended as it is believed this would best meet the stated purposes for the apparatus. In doing so, it must be recognized that accuracy and reproducibility may be sacrified. Any programmed heating tests have inherent errors due to the physical factors which creat time lags. These type of experiments are difficult to reproduce between laboratories.

It may be considered prudent to concentrate on an individual test, such as the static Bothermal experiment, from which reproducible results can be obtained, though the time to carry out such tests may be longer.

The advantages of a multi-sample apparatus should be compared with similar expenditures on a more accurate and sensitive test apparatus for

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adiabatic or other procedure. The need to separate the effects of moisture and oxidation should be considered.

The decision as to which direction to proceed is totally dependent on for what purpose the apparatus is being designed. Further discussion should be held at the start of Phase II to discuss this issue.

SPONTANEOUS COMBUSTION TEST APPARATUS
PHASE I

SECTION 6 - TEST APPARATUS FUNCTIONAL REQUIREMENTS

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FIGURES
(Following Text)

6-1 Summary of Test Conditions

TEST APPARATUS FUNCTIONAL REQUIREMENTS

6.1 GENERAL

The conclusion was reached in Section 5 that no single test fully determines the spontaneous combustion liability of a coal and that a number of different tests should be considered. In combination, the relative susceptibility of a coal may be established in a laboratory. However, extrinsic factors such as mining methods or stockpile conditions have a major influence on whether spontaneous combustion actually occurs in practice.

It is proposed that an apparatus be designed that is automated, multi-sample, and can operate in a number of different modes. It should be capable of use for isothermal tests, crossing-point or other ramped temperature tests, oxygen absorption measurements and differential thermal analysis.

A summary of the conditions used in susceptibility tests by a number of researchers is presented in Table 6-1.

The fundamental differences between these test procedures that affects the apparatus design is whether the temperature is held constant or increased in a controlled manner. It is considered that an apparatus can be designed which can operate in both modes, although accuracy may be sacrificed to get this flexibility.

6.2 NUMBER OF SAMPLES

The multi-sample apparatus should be capable of handling 4-6 samples for each test run. In addition, a reference or inert sample should be allowed for.

6.3 SAMPLE WEIGHT

Sample weight used in tests is a compromise based on several factors.

- Availability of sample; for example, with drill-cores, the amount of sample available is limited.

- Accuracy of measuring equipment. Normally heat, oxygen absorption and weight measurements can be determined more accurately with larger samples. The accuracy and sensitivity of any measuring devices influence the selection of sample weight.

- Sample size; the particle size of the sample tested has an effect on sample weight.

- Conductivity; coal is a poor thermal conductor. Temperatures can vary within a large sample making accurate measurement difficult. Heat may be slow to dissipate from a large sample to the surrounding heat sink introducing errors particularly with isothermal and differential thermal analysis tests. It is recommended that the apparatus should be constructed to handle samples in the 20-100 g range.

6.4 SAMPLE SIZE DISTRIBUTION

The size distribution of the sample is an extremely important parameter in all the tests. The smaller the particle size, the greater the exposed surface area and the greater the rate of oxidation for a particular coal. This allows faster test procedures. Banerjee and Chakravorty (1967) showed that for D.T.A. studies, the particle size of the sample could affect the shape of the resultant thermogram. Consistent results were obtained when the coal was crushed to below 0.21 mm topsize with no change on further grinding. It was thought

that use of coarser sized particles made temperature measurements inaccurate due to poor conduction.

However, use of a sized coal particle, e.g., 1.0 mm - 0.5 mm is advocated by some since it controls the surface area of the sample. Tests utilizing surface inhibitors are more readily carried out on sized material. For some tests, the packing density of the coal sample is important and a closely sized sample can give more consistency in this respect.

For apparatus design, it is recommended that the coal could either be crushed to below 0.21 mm or be a sized sample with particles up to 2 mm in size.

6.5 SAMPLE PREPARATION

The method of sample preparation is important to any oxidation tests. Fresh samples obtained from core or sample sites should be immediately placed in an atmosphere of nitrogen or other inert gas. Sample preparation should be carried out under inert conditions at the earliest opportunity.

For some isothermal procedures, the samples should be raised in temperature in an inert atmosphere prior to admitting the oxidizing atmosphere. This inerting feature needs to be considered in the test apparatus design.

Coal is more reactive in a dried state, particularly if vacuum dried in an inert atmosphere. However, one objective of the test apparatus is to compare the susceptibility of a coal at various moisture levels, both above and below its equilibrium moisture content. Therefore, it should be assumed that samples may have a wide range of moisture content intially.

It is recommended that the sample preparation procedure be separate from the automatic test apparatus under consideration. However, provision must be made to provide an inert atmosphere within the test apparatus.

6.6 SAMPLE CONTAINER

In static oxidation tests, there must be sufficient volume available to contain the oxidizing atmophere in addition to the sample. This volume depends on the test procedure used. As oxygen is absorbed into the coal, the partial pressure of oxygen reduces and the reaction slows relative to the rate it would have been at the initial pressure. The change in pressure can be determined as a measure of the amount of oxygen absorbed. The volume available for the oxidizing atmosphere will affect this pressure change.

The container must allow free circulation of the gases through the sample. At the same time, any heat produced must be dissipated as quickly as possible to the main heat sink of the surroundings. In a multi-sample set-up, the heat dissipated from one sample must not affect the ambient temperature of adjacent samples. For tests where the gases are flowing, the space around the sample can be minimized. It is recommended that the apparatus be designed to handle flowing conditions only for the oxidizing gas.

6.7 SAMPLE HEATING

The heating of the sample to predetermined temperatures and the dissipation of heat to surroundings for isothermal tests can be achieved by a number of methods.

Media used include air, water, oil, glycerine and metal cores. Shondart (1984) recommends use of a metal block. Water baths are useful for studies involving small rises in temperature, but are limited to about 90°C. Oil at higher temperatures becomes inflammable and can give off objectional vapours. Air baths suffer from poor heat transfer. The metal heat sink has the advantage that it can be completely specified in terms of dimensions and heat conductivity allowing duplication by other workers, temperatures can be closely controlled and programmed and higher temperatures can be used. The disadvantages of a metal heat sink in a multi-sample situation is the difficulty in ensuring an even temperature throughout the metal block and the complete dissipation of heat from each sample without affecting the other samples under test. At the design stage, a compromise has to be reached between the need to increase thermal capacity to eliminate these temperature variations and the need to have a responsive system under programmed heating conditions.

It is recommended that use of a metal heat-sink be investigated as a first priority during the design stage, with the alternative being circulated air if metal is found impractical. Operation over temperature range of 15°C to 250°C is required, with the temperature controlled to $\pm$0.1°C of desired values.

Programmed heating rates should be variable and range from 10°C/h to 120°C/h.

6.8 ATMOSPHERE

Various gas combinations should be available for the different test procedures proposed.

Inert gas; normally nitrogen, the inert gas stream can be used during preheating or drying stages and for specific tests.

Air; Closest atmosphere to that existing in actual conditions.

Oxygen: Use of pure oxygen accelerates the oxidation reaction and so reduces the time required to carry out a test.

Oxygen/Nitrogen; Consideration should be given to use of oxygen/-nitrogen mixtures in any proportion to study affect of oxygen proportion on susceptibility indices. This may provide a balance between test duration ad relative clarity of results.

For each gas, moisture content is a critical parameter that must be controlled if results are to be meaningful and reproducible.

It is recommended that facilities be included to provide the gas either dry or moist. In considering moist air some control of humidity is necessary. The simplest method is to saturate the gas at ambient temperature in a bubble water bath. A more sophisticated technique could be to raise the temperature of the bubble bath to match that of the sample or its surrounding heat-sink. Clearly that will be a maximum practical temperature of below 100°C at which 100% humidity can be ahieved. Humidity control for intermediate values should be considered. Precautions will have to be taken to prevent condensation of the water vapour in the gas stream during discharge from the apparatus.

Dry gas can be produced by passing it through a suitable filter.

The gases should be supplied under pressure in cylinders. Pressure and flow control will be required to suit the characteristics of the apparatus designed. It is anticipated that gas flowrates will be in the 50-200 mL/mm range.

The temperature of the inlet gas is important since the gas can either supply heat to or remove heat from the sample. Lack of consistency can lead to inconsistent test results. Ideally, the gases should be introduced at the temperature of the sample. In practice, this may prove difficult in a multi-sample apparatus so it is recommended the gas be introduced at the temperature of the sample surroundings, i.e., of the heat-sink.

6.9 MEASUREMENTS

A number of measurement devices are required to continuously monitor conditions during the tests. These include:

- Temperature of inlet gas
- Flowrate of inlet gas
- Pressure of inlet gas
- Temperatures of samples and reference
- Temperature of surrounding heat-sink
- Analysis of exit gases for carbon monoxide and oxygen contents and the provision to hook into a gas chromatograph

Not all these measurements may be required depending on the type of apparatus finally selected.

It is envisioned that all data measurements will be recorded in a central control unit which may also manipulate the data into a required format and also perform on-line control functions.

6.10 SUMMARY OF FUNCTIONAL REQUIREMENTS AND ALTERNATIVES

Inlet Gases

Composition:

- Nitrogen
- Air
- Oxygen
- Oxygen/Nitrogen Mixtures

Temperature:

- Ambient
- Preheated to sample temperature
- Preheated to bath temperature

Moisture Content:

- Dry
- 100% humidity at laboratory temperature
- 100% humidity at bath temperatures up to 100°C
- Controlled humidity to preset values

Flowrates:

- 50-200 mL/min

Samples

Number:

- 4-6 plus reference

Weight:

- 20-100 g

Size:

- Below 0.21 mm
- Sized (2-1 mm typical)

Pretreatment:

- Maintained in inert atmosphere

Measurements

Inlet Gas:

- Temperature
- Flowrate
- Pressure
- Humidity

Samples:

- Temperature
- Weight
- Heat flow to heat sink

Heat Sink:

- Temperatures

Exit Gases:

- Temperature
- Carbon Monoxide
- Oxygen
- Flow

TABLE 6-1

SPONTANEOUS COMBUSTION TEST APPARATUS

SUMMARY OF TEST CONDITIONS

				SAMPLE CONDITIONS			ATMOSPHERE CONDITIONS		
TYPE OF TEST	AUTHOR	YEAR	COUNTRY	MOISTURE CONDITION	PARTICLE SIZE (mm	SAMPLE SIZE(G)	GASES USED	FLOW RATE (ML/MIN)	TEMPERATURE DEG C
Adiabatic Calorimetry	A.S.T.M.	1951	U.S.A.	Moist	0.14-0.07	10	Air	900	20-250
Adiabatic Calorimetry	Berkowitz	1951	Australia	Dried	<0.40	40	Moist O2	1980	25-40
Adiabatic Calorimetry	Cudmore	1967	Australia	Dried	<0.075	150	N2,O2	150	40
Adiabatic Calorimetry	Elder	1965	U.S.A.	Dried	6.3	9000	O2	-	27-150
Adiabatic Calorimetry	Gray	1971	U.K.	Dried	<0.21	100	Moist Air	250	40
Adiabatic Calorimetry	Hodges	1964	U.K.	Moist.dry	<0.21	5	Air	10	20
Adiabatic Calorimetry	Hodges	1964	U.K.	Moist.dry	<0.21	2000	O2	1500	30
Adiabatic Calorimetry	Kutcha	1980	U.S.A.	Moist.dry	0.15-0.075	100	Air,N2	30	25-200
Adiabatic Calorimetry	Lee	1976	U.K.	Dry	<0.2	15	Air,N2	N.A.	60-100
Adiabatic Calorimetry	Onitsuka	1980	Japan	Moist	Variable	-	O2	3	20-200
Adiabatic Calorimetry	Singh	1986	U.K.	Moist.dry	<0.21	100	Moist,Dry Air	200	40
Crossing Point	Banerjee	1955	India	Moist	<0.21	20	Moist Air	80	20-200(30/h)
Crossing Point	Chakravorty	1956	Canada	60% R.H.	0.25-0.075	50	Air	80	20-200(30/h)
Crossing Point	Cudmore	1980	Australia	Moist	0.6-0.3	5	O2	200	120-200(120/h)
Crossing Point	Nandy	1970	India	Moist	<0.21	20	Moist Air	80	75-200
Differential Thermal Analysis	Banerjee	1967	India	Moist	<0.21	0.6	Air	-	20-200(30/h)
Dynamic Isothermal	Chamberlain	1973	U.K.	Moist	0.425-0.25	50	Air,N2	80	20-200(35/h)
Dynamic Isothermal	Shea	1972	U.S.A.	Dry	3-1.2	600	MoistO2,N2,Air	276	65
Dynamic Isothermal	Shondhart	1984	Australia	Moist.dry	-	25	O2	-	40
Ignition Temperature	Olpinski	1982	Poland	Moist	0.075-0.06	0.7	Hot Air	600	237
Isothermal Calorimetry	Battacharyya	1971	U.K.	Variable	<0.21	5	Air/N2	12.5	30
Isothermal Calorimetry	Heemskerk	1982	Netherlands	Variable	2.0-1.2	20	Air,N2,O2	-	65-85
Isothermal Calorimetry	Stott	1985	New Zealand	Moist	<0.21	14	Moist Air,N2	1	50
Isothermal Calorimetry	Stott	1960	New Zealand	Dried	2.5-0.25	3000	Moist O2,Air	1000	22
Oxygen Absorption	Carpenter	1964	Wales	Dried	0.21-0.15	20	Dry O2	0	75-115
Oxygen Absorption	Chakravorty	1966	Canada	Moist.dry	0.25-0.075	100	Air	-	30-60
Oxygen Absorption	Chamberlain	1973	U.K.	Moist	<0.21	10	Air	-	30
Oxygen Absorption	Elder	1965	U.S.A.	Moist	-	-	Air	-	30
Oxygen Absorption	Kutcha	1980	U.S.A.	Moist.dry	2.0-0.85	50	Air	-	25-100
Oxygen Absorption	Nordon	1984	Australia	Moist	3.35-0.85	40	Air	60-300	55
Oxygen Absorption	Panasenko	1974	U.S.S.R.	Dry,moist	-	-	O2	-	20
Oxygen Absorption	Sevenster	1961	New Zealand	Dried	<0.25	5	O2	-	0-100
Oxygen Absorption (IGD)	Lindenau	1977	U.S.S.R.	Moist	3.0-1.0	100	Moist Air	-	25
Oxygen Absorption(MAKII)	Lindenau	1977	U.S.S.R.	Moist	0.43-0.3	100	Moist Air	167	25-250(25/h)

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SPONTANEOUS COMBUSTION TEST APPARATUS
PHASE I

SECTION 7 - TEST APPARATUS DESIGN CONSIDERATIONS

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TEST APPARATUS DESIGN CONSIDERATIONS

7.1 GENERAL

The conclusion was reached in Section 5 that no single test, chemical or physical, fully determines the spontaneous combustion liability of a coal and that several different tests should be considered. Multiple test capability would provide the possibility of correlating the results from the various tests in the spontaneous combustion evaluation. It was suggested that the test apparatus be capable of one, or more, of the following test types:

- Isothermal tests
- Programmed temperature or crossing-point tests
- Oxygen absorption tests
- Differential thermal analysis

Section 6 reviewed the general functional requirements of a test apparatus which would be capable of performing the above tests. In addition to performing one or more of the above tests, the test apparatus should be automated to the greatest realistic extent and have multi-sample capability in the course of any one test.

While it is possible to design an instrument which is capable of performing the above tests, it must be recognized that the design will be a compromise. For example, the thermal stability desirable for an isothermal apparatus may have to be compromised to achieve the rapid heating rates desired in a programmed temperature apparatus. With careful design considerations, it should be possible to achieve most of the desired functional characteristics of the apparatus without severely compromising any one of the recommended test procedures.

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For the purposes of the ensuing discussion, it is assumed that procedures for sample preparation and particle size distribution are to be developed independently and need not be addressed here.

7.2 GENERAL CONSIDERATIONS FOR MULTI-TEST APPARATUS

The design of a single apparatus capable of performing several tests may require establishing compromise conditions such that all the tests can be performed though at less than the optimum conditions which could be achieved if only a single test was to be undertaken. With careful design considerations, it should be possible to keep the compromise conditions to a minimum.

The instrumental design considerations associated with the isothermal tests and programmed temperature, or crossing-point tests, are very compatible with one another. The thermal bath need only be held at a predetermined constant temperature, in the isothermal test, and temperature ramped from some initial temperature to a final temperature at a predetermined and constant rate for the programmed temperature tests. Such thermal baths are readily available or can be easily designed and constructed.

A true differential thermal analysis apparatus would require a radically different design that the two mentioned above. In this case, it would be desirable to utilize small samples, to ensure a uniform sample temperature and heating rate. In addition, the temperature of the sample is typically referenced to a material with well understood thermal characteristics. Because of the large sample size for which the current apparatus will be designed, there will be considerable temperature lag between the thermal bath and the coal sample due not only to the low thermal conductivity of coal, but also to the large sample size. However, by monitoring the internal temperature of the sample along with the thermal bath temperature and ratioing these to

the temperature of a reference material, such as calcified alumnina, it may be possible to obtain pseudo-differential thermal analysis data. As with the other tests used to determine the spontaneous combustion liability of coal, the interpretation of such data will rely upon experience and correlation with data obtained from other tests.

7.3 SAMPLE HEATING

As noted in Section 6, a variety of approaches and heat transfer media have been employed as thermal baths in the design of isothermal and programmed temperature instruments. It was noted that water baths are limited to a maximum temperature of approximately 90°C while oils can become inflammable at elevated temperatures. Shondart (1984) recommended the use of a metal block as a thermal bath. The advantages of a metal block, high heat capacity, high thermal conductivity and reproducibility of design, are ideal for the design of a calorimeter such as employed by Shondart. However, the high heat capacity would seriously limit the rate at which the temperature of a metal block could be raised in a ramped temperature experiment. Further, insuring a uniform heating rate and temperature throughout the block would be difficult and could limit the multi-sample capability.

Although it is recognized that circulating air baths suffer from limited heat transfer due to the low heat capacity of air, it is recommended that an air bath be considered for the test apparatus. Gas chromatographic ovens which meet essentially all of the function requirements; temprature range (15°C to 250°C), programmed heating rates (10°C/hr to 120°C/hr) and temperature control (0.1°C), are available commercially. Such ovens have a large enough internal volume to allow multi-sample capability along with the associated temperature probes, gas flow control valves and other connectors and plumbing which may be required to meet the design specifications. Further, such ovens can easily be operated at sub-ambient

temperatures, through cyrongenic cooling, as well as required for the lower temperature limit of 15°C. An additional advantage of using a gas chromatographic oven is that these ovens are commonly computer controlled which would greatly facilitate automation of the temperature selection and temperature programming functions.

With careful design considerations regarding the physical size and mass of the sample holders and associated connectors and plumbing, it should be possible to keep the thermal mass of these components to a minimum. By so doing, any temperature gradient between the sample and the heat bath resulting from the heat capacity of the sample holder components can be kept to a minimum.

7.4 SAMPLE WEIGHT

It was recommended in Section 6 that the apparatus be designed to handle samples in the 20 g to 100 g range. Assuming that the density of the coal is in the range of 1.4 - 2.0 g/cm^3, the coal volume will be in the range of 10 - 75 cm^3. Sample containers can easily be designed to handle this volume range. In addition, since the volume of coal to be studied is quite small, the design of a multi-sample apparatus will be greatly facilitated.

7.5 NUMBER OF SAMPLES

As noted above, since the individual sample volumes are quite small, 75 cm^3 maximum, the design of a multi-sample apparatus is greatly facilitated. Since the internal volume of a typical gas chromatographic oven is in excess of one cubic foot, the design of a test apparatus to accommodate the recommended 4 - 6 sample plus a reference sample should be realized.

7.6 SAMPLE CONTAINER

Since only flowing atmosphere tests are being considered, the sample containers need only be large enough to accommodate the required sample volume. Containers will be constructed from metal with consideration given to high thermal conductivity and low heat capacity to minimize any thermal gradient over the container walls between the heat bath and sample ensuring that the sample temperature is being maintained as near as possible to the bath temperature. Temperature probes will be integrated into the outlet gas connectors to allow monitoring of the temperature of these gas streams. The sample container shall also include a probe to monitor the temperature of the sample. The design will allow this probe to be placed at the center of the sample.

Consideration will be given to designing the sample containers with a sliding end cap to allow the volume of the containers to be adjusted to accommodate the desired sample volume. The container end caps will incorporate a distributor to ensure uniform gas flow through the sample and will also have screens to ensure that finely crushed samples are not swept from the container by the flowing gas.

Because of the small particle size, large sample size distribution and relatively low gas flow rates being considered here, the pressure drop across the sample container will be quite low. If it is deemed necessary, the sample containers will be provided with taps to allow a differential pressure transudcer to be placed in parallel with the sample container.

7.7 SAMPLE ATMOSPHERE

It was recommended in Section 6 that a variety of gas combinations and compositions be available for the different test procedures being

proposed. These should include an inert gas (nitrogen), air, oxygen and oxygen/nitrogen mixures in varying compositions. It was also recommended that the sample be exposed to nitrogen during any preheating or drying stages and that the change over to an oxidizing atmosphere take place at the start of the test. Gas flow rates in the range of 50 - 200 mL/min would be typical.

Individual gases will be supplied from pressurized gas cylinders and the selection for the desired gas, or gas mixture, can be easily achieved by manually, ore pneumatically, actuated valves. The latter have the advantage of being easily automated allowing for unattended operation.

Gas flow rates can be monitored through the use of calibrated gas rotameters. It is unlikely that the expense, or complexity, of mass flow controllers can be justified in this application.

Oxygen/nitrogen mixtures of any desired composition can be easily obtained through the use of calibrated gas mixers/rotameters operating at a constant backpressure. The use of gas mixers provides for infinite flexibility in selecting the desired gas composition and removes the necessity for maintaining an inventory of premixed oxygen/nitrogen gases.

An additional recommendaion is that provision be made for varying the humidity of the sample atmosphere. A dry atmosphere can be realized by passing the gas through a dessicant filter. At present, it is unknown if devices exist which are capable of providing a gas stream of given humidity at a given temperature. If such a device can be located, consideration will be given to incorporating it into the apparatus design. Saturated humidities at a given temperature can be obtained by bubbling the gas through a water bath which is being maintained at the given temperature. This bath would be independent of the sample thermal bath. Adjustment of the bath temperature would give some

control over the relative humidity. Precautions, such as heating the gas transfer line, will have to be taken to prevent water condensation upon exiting the heating bubbler. Mixing the saturated gas stream with a dry gas stream in predetermined proportions may provide a gas stream of the desired humidity. This approach can be studied should a variable humidity sample atmosphere be deemed necessary.

7.8 GAS ANALYSIS

The tests being considered utilize oxygen absorption as a measure of the spontaneous combustion liability of the coal and hence monitoring the oxygen concentration the exit gas is an integral part of the test procedure. In addition, it was recommended that the concentration of evolved carbon monoxide be monitored. The use of component selective detectors will allow the concentrations of these two gases in the sample outlet streams to be monitored in an online real-time mode. These detectors are easily calibrated, have wide dynamic range, good sensitivity and provide a voltage signal output which can be easily integrated into a computer system. It is also suggested that the oxygen content of the inlet gas streams be monitored by placing transducers in the inlet gas streams. This will provide accurate knowledge of the oxygen content of the inlet gas stream and determination of the composition of the oxygen/nitrogen mixed stream.

It was also recommended in Section 6 that provision be made for optional gas chromatographic analysis of the exit gas streams should it become necessary to have detailed knowledge of the volatile pyrolysis products resulting from heating the coal under a variety of conditions and atmospheres. Coupling a gas chromatograph to the test apparatus could be accomplished in a straight forward manner by simply placing the gas chromatograph gas sampling loop in the exit gas stream from the sample container. However, since 4 - 6 samples would be undergoing simultaneous testing, it would be necessary to incorporate

multiple multi-sample loop gas sampling valves, one multi-loop valve coupled to each sample container. Gas samples taken periodically and stored in the multiple sample loops of the gas sampling valve could then be analyzed following completion of the coal test sequence. Such a gas sampling system would be complex; however, it could be constructed from commercially available components.

7.9 APPARATUS AUTOMATION

The test apparatus design will use online instrument control and data acquisition to extent that it is realistic on a cost/performance basis. The configuration recommended employs extensive automation. In particular, each sample in the multi-sample system will be monitored for:

- sample temperature
- exit gas temperature
- exit gas oxygen content
- exit gas carbon monoxide content
- inlet gas oxygen content

The reference sample will be monitored for:

- reference material temperature
- exit gas temperature

In addition, the thermal bath temperature will be monitored.

Direct instrumental control will be limited to establishing temperature set points and programmed temperature heating rates on the oven and actuating pneumatic valves to switch from the initial inert gas to the oxidizing gas at the start of the test run. Additional instrumental

control functions such as gas flow rates or gas mixture composition would be prohibitively expensive although gas flow rates can be computer controlled through the use of mass flow controllers.

Overall, if it is assumed the test system will accommodate 6 test samples, 33 analog signals (temperatures and gas compositions) will be monitored and 6 pneumatic gas switching valves will be controlled. In addition, the temperature of the oven will be monitored and oven temperature set points and programming rates will be controlled by the computer system.

The apparatus controller can be based on a scientifically oriented microcomputer which should have both hard disk and floppy disk mass storage. The system should have graphics capability and be configured with both a printer and multipen plotter. To facilitate data acquisition and instrument control, an intelligent interface module should be employed between the computer and the test apparatus. Such equipment is available commercially from several manufacturers.

The system software should be user friendly, highly interactive and menu driven. The software should provide a variety of data output formats including print formats and plotting formats. The capability of tabulating or plotting various samples from several test runs should be included. Since variable sample sizes are possible, the ability to normalize the oxygen absorption test results to a consistent sample mass should be included.

The software system shoud be capable of establishing default values for data sampling rates and sample stabilization times. Provision should exist for the user to input such values; however, the software should check the input values for consistency with sampling rate theories and to ensure the requested values are within the system capability.

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APPENDIX A

A Low Temperature Reaction Calorimeter of the Calvet Type for the Measurement of the Heat of Oxidation of Coal

by

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A low temperature reaction calorimeter of the Calvet type for the measurement of the heat of oxidation of coal

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Abstract. A new calorimeter system is described, in which the rate of reaction is determined simultaneously with the heat of reaction. The system operates near ambient temperature and is particularly suitable for measurement of air/coal interactions which are responsible for self-heating and spontaneous combustion. These interactions are characterised by an extremely slow evolution of heat of the order of about 5×10^{-6} watts per g of coal which changes with time requiring the instrument to remain stable over a period of several weeks. The instrument may also be suitable for investigations of self-heating of other materials which are commonly stockpiled.

1. Introduction

Coal and many other materials (bagasse, sulphide ores, etc) which are stockpiled can undergo oxidation reactions with resultant evolution of heat. At best, these 'weathering' processes lead to loss of desirable properties and, at worst, to substantial self-heating or even to spontaneous combustion. These reactions are difficult to investigate as they are exceedingly slow and can only be observed when the material is present in large quantities occupying considerable bulk. In such cases heat generation cannot be compensated by heat losses.

It is of interest, therefore, to be able to measure the heat output of these reactions directly on small quantities of material close to the temperature and conditions at which they occur in practice. In many cases one has to deal with a naturally occurring substance which has an intrinsic heterogeneity for which the starting point of the oxidative 'weathering' reaction is ill-defined. It was the aim, therefore, to design a calorimeter system in which the overall rate of reaction with respect to oxygen could be measured simultaneously with the heat output, avoiding uncertainties in the two measurements introduced by sample variations, treatment or age.

Adiabatic calorimetry has been used previously to determine the susceptibility of coals to self-heating (Davis and Byrne 1924, Elder *et al* 1945, Heusinger and Munzner 1964) but the method requires knowledge of the specific heats of the coals over a range of temperature. Furthermore, the sensitivity and accuracy of the adiabatic control systems used required appreciable initial temperatures for the systems to exhibit self-heating (70 °C or higher).

A number of calorimeters have been described which operate on isothermal principles (to within about 5 to 10 °C) in which the steady state temperature drop across the coal itself (Newman 1956), the drop across an external insulating layer (Van Doornum 1954) or metal wires (Stott 1956) has been employed to measure the rate of heat generation. A few calorimeters have been constructed (Hodges and Acherjee 1965) or commercially produced (Ettinger *et al* 1981, Saranchuk *et al* 1982), which operate on the technique first described by Calvet and Prat (1963) which follows, more closely, isothermal principles. Of these latter instruments the one described by Hodges and Acherjee (1965) did not compensate for thermostat temperature fluctuations by employing a reference (twin) calorimeter while the other two were micro-calorimeters (8 cm^3 sample volume) whose type and design description are not easily traced. Only one of the latter two was used in a system which also monitored the oxidant flow.

The calorimeter to be described here is also based on the Calvet type (but of novel design) and seeks a compromise between sample size, which is required for accuracy in determining reaction rate, thermal sensitivity, speed of response and long term stability. The rate of oxidation of coal near ambient temperature can vary over an enormous range about 1000:1 (Sondreal and Ellman 1974) depending on type, age and particle size. However, only the more reactive coals with reaction rates of more than 5×10^{-10} s^{-1} (g of O_2 per g of coal per s) are of interest as they alone show problems during stockpiling. Similarly, using typical values for heat generation during 'weathering', the calorimeter should be able to measure a heat output of at least about 5×10^{-6} watts per g of coal. Taking account of both the rate of oxygen consumption and the heat of reaction, present day limitations imposed by the chemical analysis and control of the gas stream dictate a sample of about 25–50 g of coal and sample volume of about 60 cm^3.

2. Theoretical principles of operation

When measuring the heat of an exothermic reaction care has to be exercised not to operate too closely to the 'critical temperature' to avoid a 'thermal run-away'. The critical temperature depends on the rate of reaction, shape and size of the calorimeter vessel and on the oxygen supply (Boddington *et al* 1983). For a coal of medium reactivity this limits use of the present calorimeter to a maximum temperature of about 120 °C.

If one assumes, as a first approximation, that heat is produced at a constant rate A_0, in an infinite cylinder of radius a, of thermal conductivity K, and diffusivity κ, then, for Cauchy boundary conditions, the temperature difference between the cylinder and its surroundings is given by (Carslaw and Jaeger 1950)

$$T = \frac{A_0 a^2}{4K}\left(1 - \frac{r^2}{a^2} + \frac{2}{ah}\right) - \frac{2hA_0}{ah}\sum_{n=1}^{\infty} \exp(-\kappa\alpha_n^2 t)\,\frac{J_0(r\alpha_n)}{\alpha_n^2(h^2 + \alpha_n^2)J_0(a\alpha_n)} \qquad (1)$$

$T = 0$ at $r = 0$ and $t = 0$

$$\frac{\partial T}{\partial r} + h(T - T_0) = 0 \text{ at } r = a \text{ and } t > 0. \qquad (2)$$

The α_n are the roots of the transcendental equation

$$\alpha J_1(a\alpha) = hJ_0(a\alpha) \qquad (3)$$

and J_0 and J_1 are the Bessel functions of zero and first order.

The quantity h in the boundary condition (2) is the ratio

$$h = \frac{H}{K}$$

where H is the 'conductivity' of the boundary layer and equation (2) in the form

$$-K\frac{dT}{dr} = H(T - T_0) \qquad (2a)$$

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may be interpreted as the equality of the thermal flux passing into, and out of, the surface of the cylinder. H can be determined approximately during calibration when, instead of coal, an electric heater surrounded by an aluminium core is placed in the calorimeter vessel. Under these conditions the electric power dissipated by the heater produces a constant flux across the air gap of the calorimeter (to be discussed later) and measurement of the temperature difference, $v - v_0$, across the gap permits determination of H.

At thermal equilibrium ($t \to \infty$) the temperature at the centre of the cylinder is

$$v_{r=0} = \frac{A_0 a(ah - 2)}{4Kh}$$

and at the surface

$$v_{r=a} = \frac{A_0 a}{2Kh}$$

so that the temperature difference between centre and surface is

$$\Delta v = \frac{A_0 a}{K}\left(\frac{1}{h} - \frac{a}{4}\right). \qquad (4)$$

K may be known from general data or can be determined in a subsidiary measurement and A_0, of course, is approximated by the main calorimetric measurement. Thus, to a close approximation, the difference between the centre and the boundary of the coal charge in the calorimeter vessel can be estimated and its proximity to criticality judged (Boddington *et al* 1983).

3. The calorimeter system

Although the calorimeter is the central instrument to be described, other components in addition are necessary for its successful operation. These include gas metering and temperature control of the thermostat and are discussed below.

3.1. Gas metering

Gas for the reaction (here air) is supplied from a commercial cylinder and led via a T piece to a rotameter which exhausts to atmosphere. The remaining branch of the T, being under slight pressure, supplies a peristaltic pump (Cole-Parmer Instrument Company, 'Masterflex' model, pump head 7014-20, Tygon tubing, 0.0655" ID and 0.1945" OD) which is driven via a 10:1 reduction gear box by an electronically adjustable stepping motor (Slosyn, type SS50-1008, 50 in. oz. torque with 200 steps per rev.). The revolutions of the motor are counted, and integrated to obtain the flow rate and total gas flow to the calorimeter. The delivery of the pump is calibrated using air and a 'soap bubble' meter. Gases deficient in oxygen should not be used as they may introduce errors due to diffusional effects across the soap film. Pumping rates as low as 1 $mm^3 s^{-1}$ have been used.

After passing through the calorimeter the chemical composition of the gas stream is analysed by automated gas chromatography. The component of interest, namely oxygen, is measured with reference to the inert component, nitrogen. The pumping rate is adjusted so that reaction with the coal results in only a small drop in oxygen concentration (for air, say, 1 to 2%) and hence the concentration difference between inlet and outlet streams together with the flow rate permit calculation of the amount of oxygen which has combined with the coal. By permitting only a small drop in the concentration to occur, the mean concentration of oxygen taking part in the reaction is known within reasonable limits.

A characteristic of the system is the slow displacement time for the gas. At a low flow rate of, say, 3 $mm^3 s^{-1}$ it takes longer than 12 hours to change the concentration of oxygen in the calorimeter.

This slow response of the system to changes in concentration is not as severe as may appear, as coal is a porous substance which at any rate depends on the diffusion time of oxygen into individual particles. If faster changes are required, the system can be 'flushed' with gas at a new concentration before reverting to the optimum measuring flow rate.

3.2. The calorimeter

The calorimeter is based on the Calvet type in which the heat flux produced by the reaction is measured as a temperature difference across an air gap between concentric cylinders, the inner one holding the sample and the outer one being essentially at a constant temperature.

The inner cylinder has a removable insert, also in the form of a hollow cylinder, which holds the coal sample. During operation fresh oxidising gas enters at the bottom of the cylinder, passes between the coal particles and leaves from the top via a tube to a gas chromatograph. Due to the very low flow rate used an even gas distribution over the coal (at right angles to the axis of the cylinder) is achieved by molecular diffusion.

An elevation and plan view of the mechanical construction of the calorimeter is shown in figures 1 and 2. The sample is held in the removable brass tube, A, (23 mm ID and 152 mm long) provided with wire mesh at the bottom which retains the coal (or other) sample. It can be exchanged for a close fitting aluminium rod containing a 4-terminal heater for calibration purposes. The brass tube (or the heater) is contained in the inner brass cylinder, B, (23.5 mm ID, 34 mm OD and 169 mm long) of the calorimeter provided with a gas inlet, C, at the bottom. The cylinder is held in place by reinforced fibre glass board at the two ends. D. The sample container, A, is closed by a spring loaded plug, E, with gas outlet, F. Viton rubber washers, G, provide gas tight seals. The outer cylindrical block of the calorimeter is in three parts, a base, H, carrying a small tube, J, with the electrical connections to the thermopile, the main body, K (48 mm ID, 71 mm OD and 160 mm long) and a cap, L, which holds the inner vessel (spring loading) and gas outlet in place. When calibrating the calorimeter, the heater leads are passed through the gas outlet tube, F.

The temperature difference across the air gap is measured by a copper/constantan thermopile which departs substantially from the conventional Calvet design. It is formed by winding 68 turns of 0.125 mm dia. constantan wire on a tube made from 0.38 mm thick reinforced Teflon cloth, 6 mm dia. and 152 mm long. Copper is then plated (Benzinger and Kitzinger 1963) on one half of the winding, parallel to the axis, so that each turn of the winding forms a copper constantan couple and 68 are connected in series. Uniformity of plating was assisted by using an ultrasonically agitated plating bath and providing current leads to several sections of the constantan spiral. Plating was continued until a predetermined reduction in resistance was obtained representing a compromise between low thermal conductance and high thermoelectric output (about 0.0015 mm film thickness).

Fourteen of these tubes with plated windings were inserted into the air gap (see figure 2), each being rotated around its axis until the copper/constantan junctions were as close to the opposite faces of the gap as possible. A 1.6 mm thick balsa wood wedge was then inserted into the centre of each tube pressing the junctions against the insulated (Teflon cloth) walls of the gap. The tubular-windings were connected in series, forming a thermopile, which had an electrical resistance of about 620 ohms and consisted of 952 thermocouples each having an output of about 26 $\mu V\,°C^{-1}$.

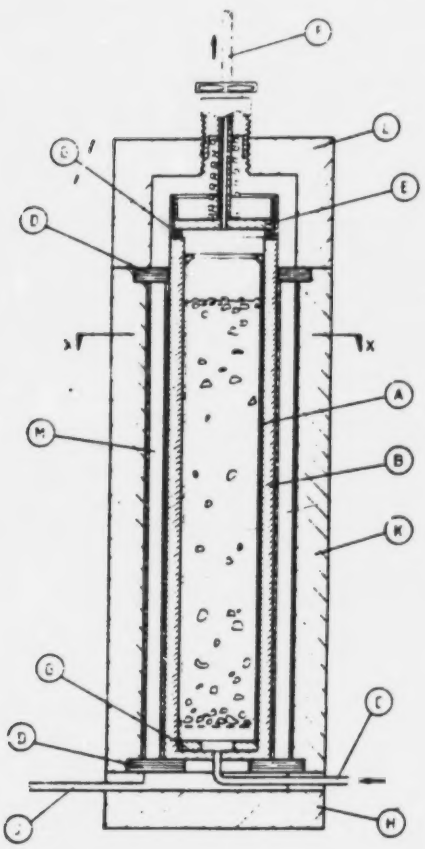

Figure 1. Elevation of calorimeter: A. removable brass tube; B. inner brass cylinder; C. gas inlet; D. reinforced fibre glass board; E. spring loaded plug; F. gas outlet; G. rubber washers; H. base; J. tube for electrical connections; K. main body; L. cap; M. thermopile.

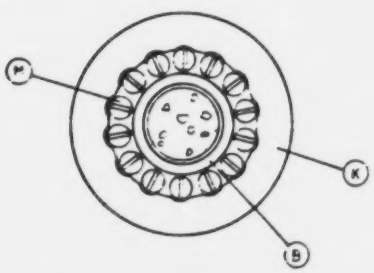

Figure 2. Section across X–X: B. inner brass cylinder; K. main body; M. thermopile.

The successful operation of the system depends on the outer calorimeter block being at steady temperature. Because of the high sensitivity of the thermopile and limitations inherent in the thermostat, the system is built up of two identical calorimeters with their thermopiles connected in opposition so that external fluctuations in temperature tend to be cancelled. This requires matching the sensitivities of the calorimeters and exposing them to the same spatial and temporal thermal environments. The sensitivities can be matched easily by providing the more sensitive calorimeter with a shunt (approx. 10 000 Ω) which is used as an adjustable potentiometer to reduce the electrical output to the required value. The output of the twin calorimeter (using one as a reference) is about 50 μV mW^{-1} and can be monitored directly using a 1 mV FSD recorder having an input impedance of 10^8 ohms or higher. The output can be determined to the nearest μV using a suitable meter. Thus, the sensitivity of the calorimeter system is about 10^{-6} watts per g of coal. The present limitation of the system is the temperature control of the thermostat.

To further compensate for thermostat fluctuations, the two calorimeters were placed close together in a common sand bath maintaining a layer of sand of 30 mm thickness between the calorimeters and the circulating air of the thermostat. This arrangement represents a compromise between building a twin calorimeter in the same metal envelope which would have an extremely long time constant and close thermal coupling and the present arrangement where the coupling is less but the time constant shorter (about 16 hours). The presence of sand introduces a thermal resistance which, together with the heat capacity of the calorimeters, produces a damping of short term temperature fluctuations introduced by the thermostat control.

3.3. The thermostat

The quality of the thermostat plays a central role in the operation of Calvet type calorimeters. This is particularly true when the heat output of slow reactions is monitored which may require measurements extending over many weeks. Short term fluctuations in temperature are of no consequence as they are damped out by the thermal inertia of the metal calorimeters and the resistance of the envelope. Medium term stability, comparable to the time constant of the calorimeter, is vital. Long term fluctuations are again compensated by the twin system.

The thermostat is a 610 × 610 × 950 mm high metal enclosure provided with 50 mm of lagging and a 305 mm fan blade rotating at about 1400 RPM. About 100 mm directly under the fan are two 600 W finned heaters and, at a further 50 mm, a commercial, 100 Ω, platinum resistance thermometer. The temperature of the air circulating in the oven is controlled by 'reading' the resistance of the thermometer with a programmable digital multimeter (Keithley, 192 Programmable DMM with 5½ digit display) and comparing it with a digitally set reference temperature. The data acquisition and comparison is performed once every second by an Apple microcomputer which operates a simple on/off mode solid state switch. The switching cycle repeats about once every 50 seconds and power delivered during the 'on' period is adjusted to be about 50% of the full cycle. More complicated control functions were programmed (proportional, integral and derivative) but did not seem to improve the general performance. Although the fluctuations of the temperature of the air in the thermostat are ±1 °C, the switching times are sufficiently short to be damped out by the combined thermal resistance and capacity of the calorimeter system. No fluctuations are observable in the output of the differential thermopile on the μV level. The quality of the control is determined entirely by the stability of the resistance thermometer and by the circuitry in the digital multimeter.

3.4. Some results

In a typical application 40 g of freshly crushed (size fraction −3.35 + 0.85 mm) coal was used to measure the rate of oxygen fixation and heat evolution at 55 °C. It took about 24 hours for thermostat, sand bath and twin calorimeters to come to thermal

equilibrium. The rate of oxygen consumption during the following 13 days is shown in figure 3 while the corresponding heat evolution is shown in figure 4. Both measurements indicate a monotonic decrease in the rate with the scatter of experimental points sufficiently small to permit extension of the experiment over a much longer period.

It is also possible, using equation (4), to calculate the temperature difference between the centre of the coal and the nominal calorimeter temperature to make sure that no thermal run-away occurs. For the experiment depicted in figure 4 the heat generation after one day is 1.25×10^{-4} W g^{-1} or, at a packing density of coal of 0.8 g cm^{-3}, a volumetric heat generation, A_0, of 1.0×10^{-4} W cm^{-3}. Using a value of thermal conductivity, K, for the coal/air mixture of 1.1×10^{-3} W cm^{-1}K^{-1} and a value for H obtained from a calibration experiment, h was found to be 0.12 cm^{-1}. Using these values in equation (4) gives a temperature rise, V, at the centre of the coal of 0.84 °C. This is well removed from the critical temperature rise in a cylinder. In the present case this central temperature rise is about 38 °C (Boddington *et al* 1971).

Thus, the calorimeter system is well suited to measure the important oxygen consumption and heat generating characteristic of reactive coals near ambient temperature. The instrument, or a slight modification of it, may have wider application to other materials of similar properties.

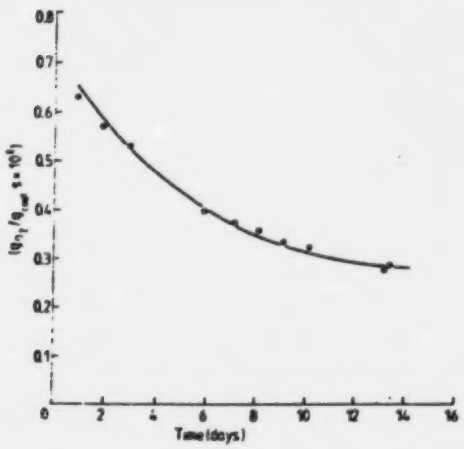

Figure 3. Rate of oxygen consumption against time.

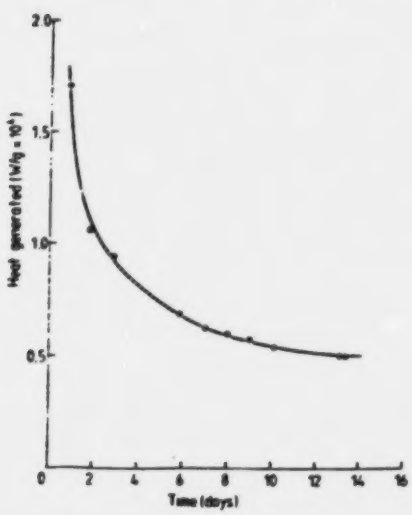

Figure 4. Rate of heat generation against time.

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APPENDIX B

Calorimeter Design and the Assessment of Self-Heating in Coal

by

J.A. Shonhardt

Calorimeter design and the assessment of self heating in coal

J.A. Shonhardt[1]

Introduction

The problem of the occurrence of self heating and spontaneous combustion during the mining, storage and transportation of coal has been the subject of research work for many decades. The research has followed two avenues; first, investigations of intrinsic coal properties such as rank, particle size, volatiles, mineral matter, moisture content and so on; second, those of an environmental nature such as temperature, gas flow, humidity of the ventilation air, packing density and range of particle size to name only a few.

Investigation of the contribution of each of the above to the overall process generally makes use of some elevated temperature method to reduce the long incubation times frequently encountered during coal handling. These may vary from up to several months in the case of stock piles to a few days in the laboratory situation.

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There are three main approaches used in the laboratory:
(a) Crossing point methods – in which coal is heated in a reaction vessel at a constant rate and the temperature of the coal and the vessel plotted simultaneously. The heating rate of the coal lags behind that of the container until self heating results in an increase in coal heating rate, until finally the heating rate of the container is exceeded at the crossing point temperature. This temperature is related to the reactivity and ultimately the self heating tendency of the coal.
(b) Isothermal methods, in which the temperature of the coal is regulated by external means to a predetermined temperature and reaction rates studied.
(c) Adiabatic methods, in which heat transfer to or from coal under test is virtually eliminated.

It was decided to employ an adiabatic test apparatus to study self heating behaviour as the conditions thus set up most closely resembled those prevailing in situ underground or in a large coal stockpile than with methods (a) or (b). Thermal conductivity in a large mass of coal is very poor and the adiabatic method is regarded as being the most realistic representation of this particular environment compared with the other approaches mentioned.

Calorimeter design

By definition an adiabatic system is one in which no heat is gained or lost by the reacting substance. This is accomplished by designing the calorimeter so that the temperature of the surroundings is continuously adjusted to match that in the sample chamber. The surroundings used in calorimeters of this type have generally been one of three types:
(a) water bath
(b) oil bath
(c) air bath.

The first of these, the water bath, is quite satisfactory for studies of reactions involving small temperature rises but is obviously not suitable if the temperatures approach the boiling point of water. Oil baths have been used in an effort to increase the versatility of the instrument, as have air baths. Oil at high temperatures, however, has

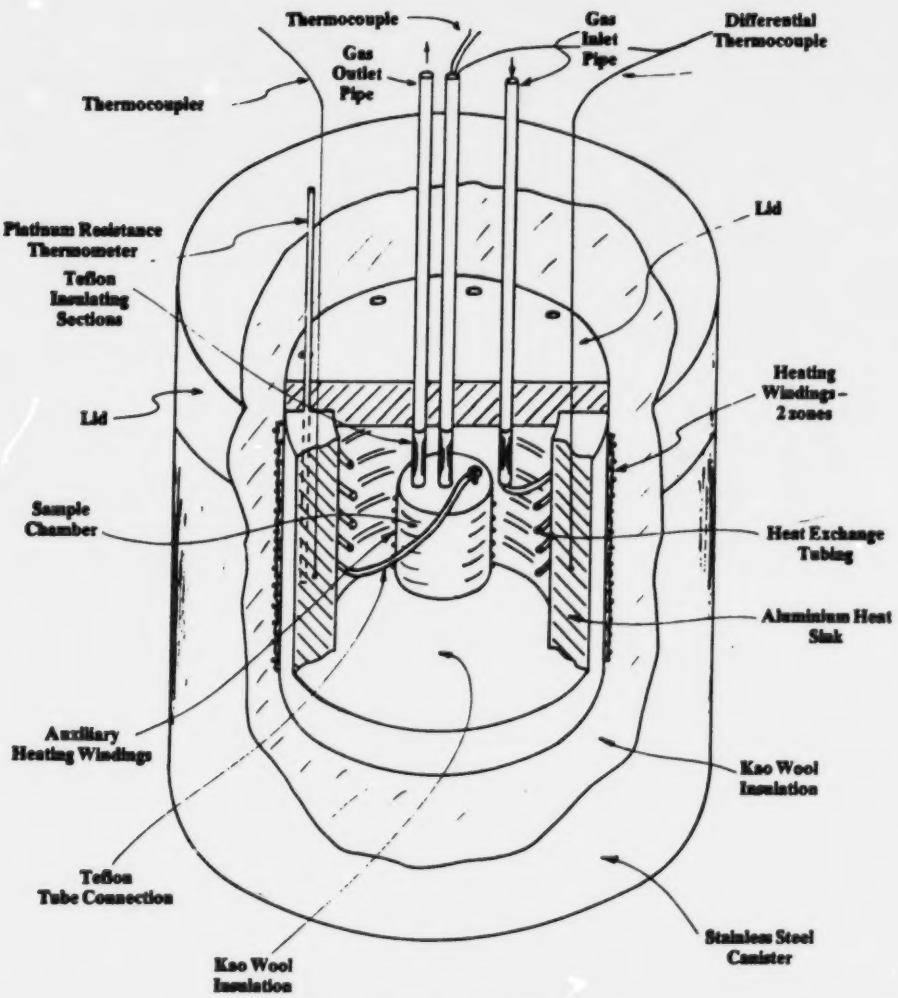

Fig. 1 Cut away view of Calorimeter

undesirable characteristics such as inflammability and objectionable vapours, and air baths, whilst eliminating the hazards mentioned, suffer from poor heat transfer, making it difficult to maintain adiabatic conditions during periods of rapid heat evolution.

Taking all these problems into consideration it was decided to use a metal block as the surrounding medium. This has the following advantages when compared with the water, oil or air bath systems:

(1) The metal heat sink can be completely specified in terms of dimensions and heat conductivity, thereby allowing exact duplication by other research workers with the attendant possibility of a comparison of results and the co-operative accumulation of a data base.

(2) Temperature fluctuations due to switching of heating elements can be effectively absorbed by taking advantage of the large heat capacity of a massive metal sink.

(3) As in the case of the air bath system, use of metal allows freedom in the choice of whatever thermal cycle is desired in the investigation. In this work it has been a major advantage to be able to operate well above 100°C when dealing with the less reactive coals.

(4) A further sophistication this type of calorimeter possesses over the air bath system is that it is possible to use powerful heating elements to supply sufficient heat to maintain adiabatic conditions in the final stages of self heating when the coal has become committed to reaching combustion temperatures. This means that reliability can be achieved and credence given to measurements of heat evolution.

Some limitations are associated with the use of a metal heat sink. These are due mainly to the conflict which exists between the need to increase thermal capacity to eliminate temperature fluctuations and the need to have a responsive system to follow abrupt temperature changes when these occur. A further drawback to the approach lies in the difficulty of attaching heating windings to the complete exterior surface of the cylindrically shaped vessel so that reliance must be placed on the conductivity of the metal to obviate the effects of uneven heating.

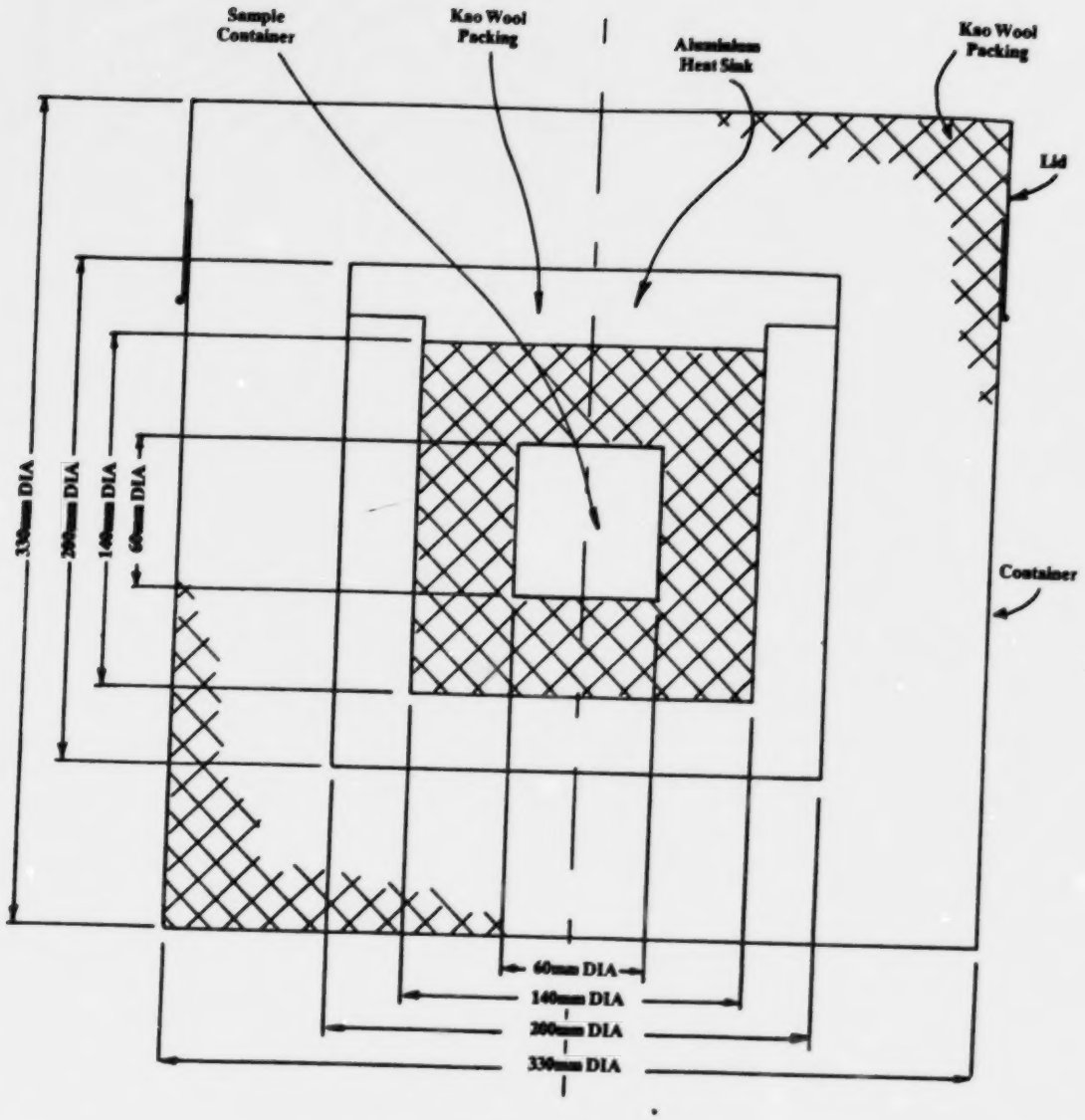

Fig. 2 Sectional view of Calorimeter

Construction details of the calorimeter

The calorimeter heat sink was machined from an 8 inch (203 mm) diameter aluminium billet. The finished heat sink (Figures 1 to 5) was cylindrical in shape with 30 mm thick walls and lid, the latter being secured by set screws. The lid gives access to a sample chamber centrally machined inside the heat sink. Rings of kao-wool alumina refractory wool were used to insulate a sample container situated in the centre of the chamber. This was made from a cut-off 100 ml pyrex beaker, ground and lapped to give a gas-tight seal against a light aluminium lid. Two Chromel-Alumel type K thermocouples and one half of a differential thermocouple were carried into the sample container by means of a brass tube and terminated in a brass heat sink in the coal. The heat sink was made of four thin blades of brass, silver soldered to the central tube, and extending almost to the glass walls of the sample chamber. This was designed so as to allow the thermocouples to look at an average temperature for the coal mass.

The temperature measuring system was calibrated periodically at 100°C with boiling water and a mercury thermometer. The outputs of the thermocouples were compensated for cold junction variations by an electronic circuit based on an AD595 microchip, and the resulting signals were recorded continuously on a 6 channel strip chart recorder.

This records the temperatures of the coal, the aluminium heat sink and

Fig 3 Aluminium heat sink

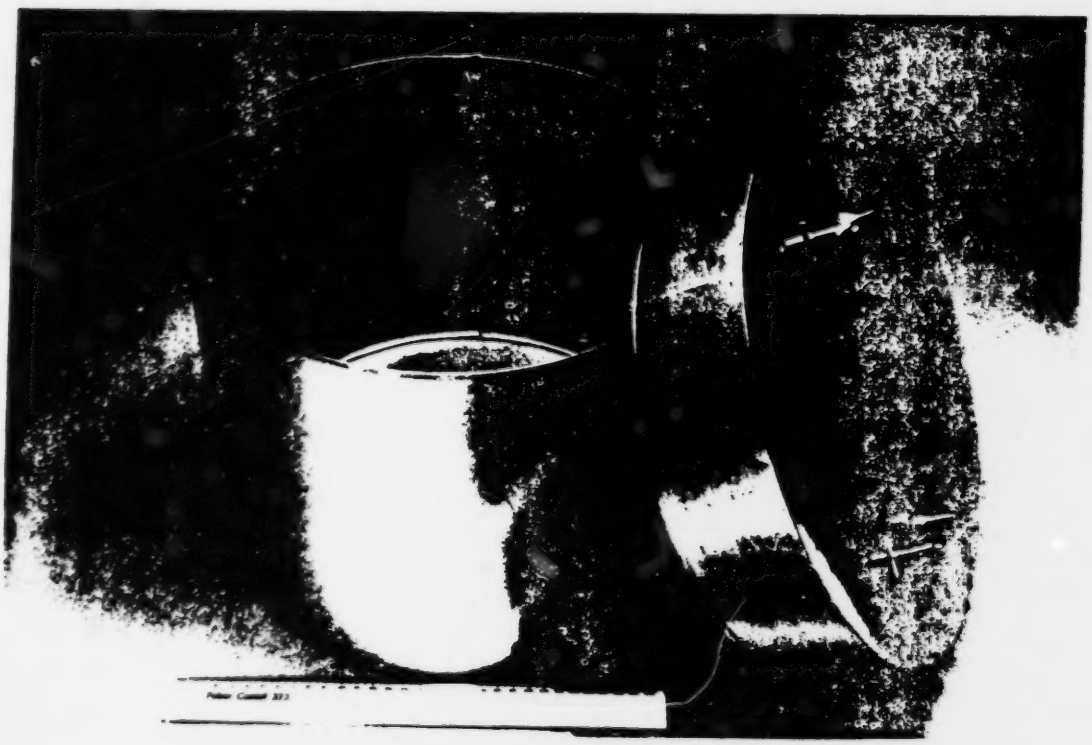

Fig 4 Stainless steel canister

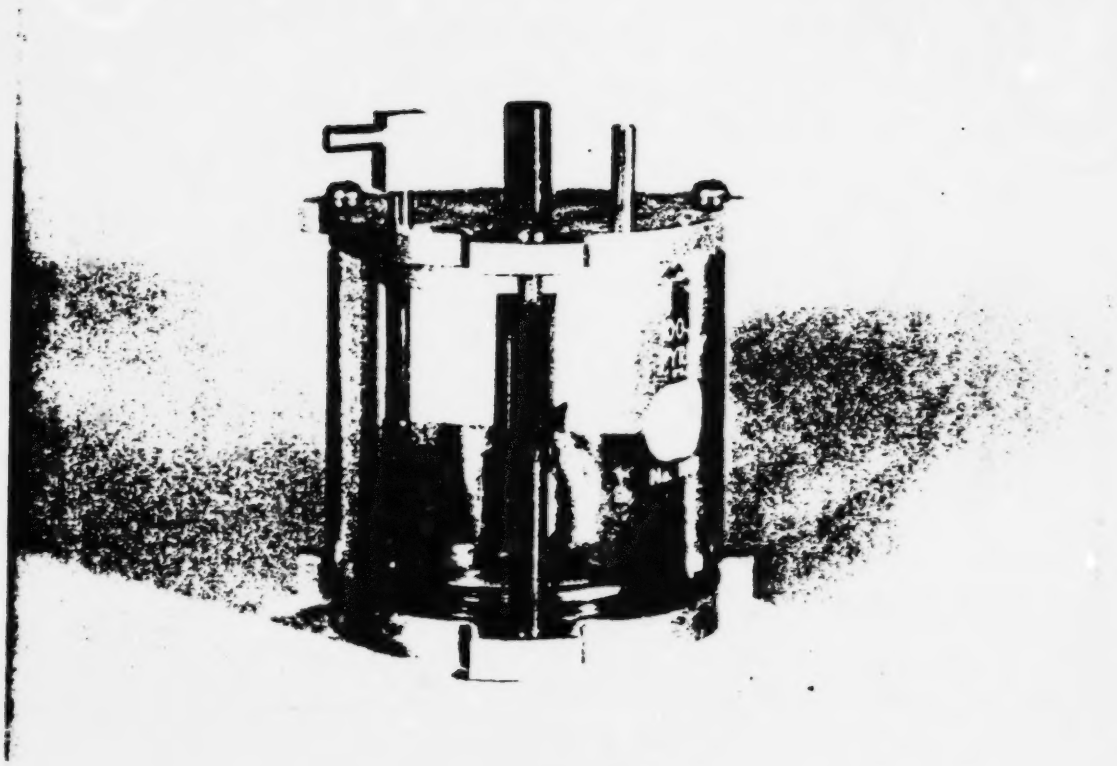

Fig. 5 Sample chamber

the water temperature of a water bath humidifier.

The heat sink is heated with two nichrome windings on the cylindrical surface and controlled by two Leeds and Northrup Electromax III Controllers. One controller regulates the incubation temperature of the test by means of a platinum resistance thermometer in the heat sink, while the other, by means of a differential thermocouple controls the heat sink temperature during self heating to maintain adiabatic conditions during periods of rising temperature.

A heating element on the sample chamber serves two purposes: calibration of the complete system is done using accurately controlled currents through this resistance and rapid testing can be done using a small heat input from the resistance winding to unbalance the adiabatic system slightly, producing a linear temperature increase with a constant input from the auxiliary heating resistance. Calibration curves produced by this method are shown in Figure 6 and derived from the experimental values in Table I. The calibration curve is a plot of heating rate $\frac{\Delta T}{\Delta t}$ vs Heating current^2, equivalent to heat input I^2R.

The heat capacity of the calorimeter was calculated using the method of Lee & Wardropper (1) as follows:

TABLE I – CALIBRATION DATA

Heating Current mA	I^2 *x 10^6 A*	*Thermocouple Readings*				*Δ°C*	*Δt Min*	*Heating Rate* $x\,10^3\,\frac{\Delta T}{\Delta t}$
		Couple No. 1		*Couple No. 2*				
		MV_1	*°C_1*	*MV_2*	*°C_2*			
10	100	1.62	40.3	1.63	40.5	0.2	75	2.67
20	400	1.63	40.5	1.64	40.8	0.3	90	3.33
25	625	1.64	40.8	1.66	41.3	0.5	85	5.88
30	900	1.66	41.3	1.67	41.5	0.2	70	2.86
35	1,225	1.67	41.5	1.68	41.8	0.3	80	3.75
40	1,600	1.68	41.8	1.72	42.8	1.0	95	10.53
60	3,600	1.71	42.3	1.76	43.8	1.5	60	25.0
70	4,900	1.76	43.8	1.94	48.0	4.2	145	28.97
80	6,400	1.94	48.0	2.01	49.8	1.8	60	30.0
90	8,100	2.01	49.8	2.15	53.3	3.5	75	46.67
100	10,000	2.15	53.3	2.30	56.8	3.5	70	50.0
120	14,400	2.30	56.8	2.50	61.8	5	60	80.33
150	22,500	1.85	46.0	2.30	56.8	10.8	85	127.06
200	40,000	2.43	60.0	2.68	66.0	6.0	40	150.0
250	62,500	2.81	69.3	3.93	96.3	27.0	85	317.65
300	90,000	4.06	99.0	5.36	130.8	31.8	70	454.2

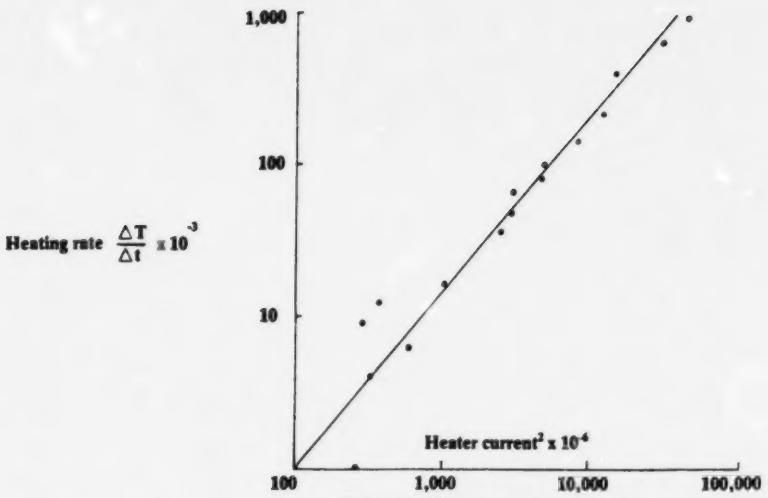

Fig. 6 Calibration curve

$$E = \text{Rate of heat input} \times \frac{\Delta t}{\Delta T}$$

at any point on the curve, say 120 MA, using a 15 ohm heater resistance,

$$E = 0.0144 \times 15 \times 60 \times \frac{60}{5}$$

$$= 151.2 \text{ Joules/°C}$$

This ranges from 137 Joules/°C at 40 MA to 178 Joules/°C at 300 MA.

The electrical circuit diagram, Figure 7, shows the elements of the system used. An upper temperature limit control, 9 on the diagram, uses a limit switch operated by the pen drive mechanism in the chart recorder to cut off all power and gas flow when the acceptable temperature limit is exceeded. Variacs are included in each element circuit to aid in adjustment of controller characteristics. The gas flow system is shown in Figure 8, with the humidifier consisting of dreschel bottles and sintered glass spargers, the humidity of the outlet gas being controlled by use of saturated solutions of various salts in the bottles to maintain equilibrium moisture levels. The solenoid cut off valve is essential to stop oxygen flow when the upper limit of temperature is reached thus preventing burn-up of the test cell.

Operation of the calorimeter

The instrument was designed to be able to operate in both the incubation mode and the rising temperature mode.

The first involves heating a 25 gm sample of coal to a predetermined temperature, commonly 40°C, in a nitrogen atmosphere, then incubating it in oxygen and observing its self heating behaviour (if any) while maintaining adiabatic conditions. The oxygen atmosphere may be humidified or dry; the coal may have moisture "as received" or be vacuum dried to constant weight at 40°C.

The gas flow rate is kept constant during testing by adjustment to constant value using the appropriate flow meter.

The temperatures of the coal sample, calorimeter heat sink and humidifier are recorded on the chart for the duration of the test.

The time required to complete this test can vary from approximately two days for a very reactive coal to weeks for one that is less reactive.

The second testing mode is basically that used above with the addition of a heat source in the sample vessel which provides for the injection of heat at a constant rate. As a result of the calorimeter control system attempting to preserve adiabatic conditions, a linear heating rate is imposed on the sample and any deviations from linearity are due solely to heat production in the coal itself.

Conclusions

The design of the calorimeter is such that it allows for rapid testing in a ramping temperature mode, while still allowing for functioning as a purely adiabatic apparatus. The ramping method has notable advantages in that it is sufficiently sensitive to differentiate between levels of reactivity in coals in the manner of the adiabatic method, but does so in times which rival that of the crossing point approach while at the same time avoiding the lack of sensitivity inherent in the latter methods.

Fail safe systems incorporated in the design allow for its operation unattended, with gas and electricity cutoffs preventing damage from runaway combustion. Frequency of testing need only be limited by the need to allow a cooling down period for the heat sink, and this could be eliminated by the use of two identical vessels and changing from one to the other as necessary, made possible by the use of the metal heat sink readily allowing duplication. This leads to the obvious conclusion that duplication could be used to advantage in allowing workers in diverse localities to compare test results, since standardisation is not difficult, and a data base on Australian coals and their relative tendencies to spontaneous heating could be catalogued.

Reference

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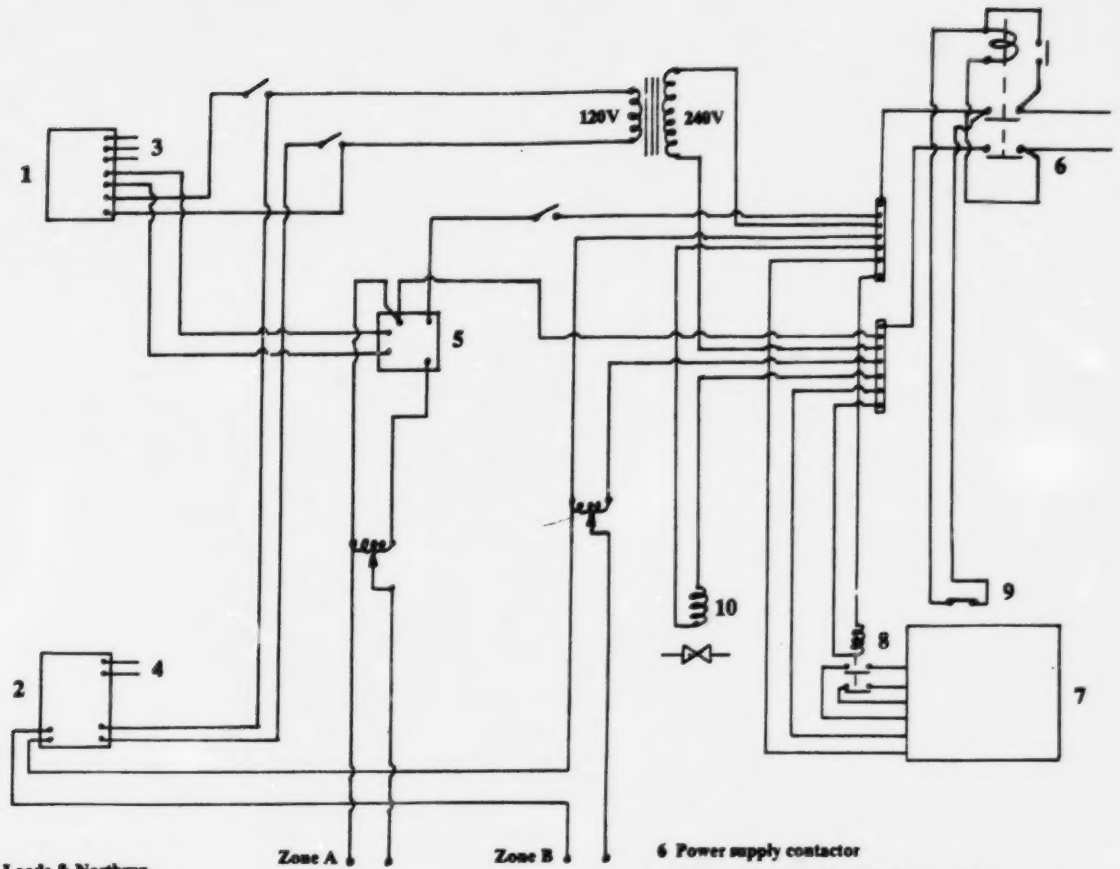

1, 2 Leeds & Northrup Electromax III controller
3 Connections to platinum resistance thermometer
4 Connections to differential thermocouple
5 Zero voltage unit – solid state switching device
6 Power supply contactor
7 Honeywell brown class 15 chart recorder
8 Chart drive motor control relay
9 Over temperature cut off control
10 Solenoid operated gas cut off valve

Fig. 7 Circuit diagram

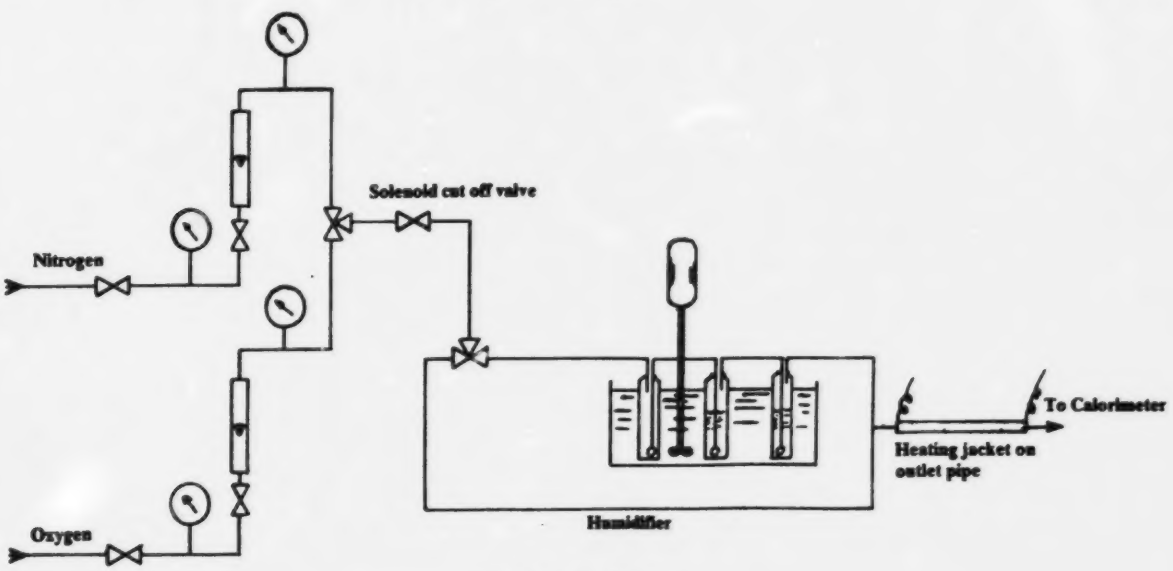

Fig. 8 Gas flow diagram

APPENDIX C

Assessment of Coal for Susceptibility to Spontaneous Combustion

A Practical System of Classifying Coal Seams Liable to Spontaneous Combustion

by
R.N. Singh

Assessment of Coal for Susceptibility to Spontaneous Combustion

by

R. N. Singh

B.Sc., M. Eng., Ph. D., C. Eng., F.I. Min. E., F.I.E., M.I.M.M.

25th November 1986

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(iii) **Current laboratory techniques *not used* in the U.K. for assessing the susceptibility of coals to spontaneous combustion.**

(iv) **Current laboratory techniques *used* in the U.K. for assessing the susceptibility of coals to spontaneous combustion.**

(v) **An opinion as to the best method, e.g. iso-thermal, adiabatic, gravimetric, oxygen absorbtion, etc.**

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(ix) **Appendix 1**

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A2 - Crossing Point Temperature Method.
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1 INTRODUCTION

A large number of intrinsic and extrinsic factors influence the liability of coal to spontaneous combustion and consequently, a number of systems have been devised in the past for the determination of spontaneous combustion risk classifiction of coal seams.

An evaluation of the spontaneous combustion hazard of coal seams requires the following considerations;

(i) Intrinsic factors which are inherent characteristics of the coal and are beyond control of the mine operators.

(ii) Extrinsic factors

(a) Geological features of coal seams
(b) Mining practice which can be controlled with forward planning and mine design. Table 1 lists some crucical factors contributing to the spontaneous combustion of coal. Intrinsic factors are responsible for a coal to be liable to heating but extrinsic factors promote its occurence. Thus by controlling extrinsic factors a coal which is inherently liable to spontaneous combustion can be safely mined, stockpiled and utilized. Coals which are not liable to heating can also catch fire if extrinsic factors are not controlled (Atkinson 1983).

2 TECHNIQUES OF DETERMINING LIABILITY OF COALS TO SPONTANEOUS COMBUSTION

In the past, two distinct approaches have been used for determining the susceptibility of coals to spontaneous combustion.

- Laboratory Methods
- Practical Methods

2.1 Laboratory Methods

These methods fall into three main groups

(i) Studies of the chemistry of the oxidation process
(ii) Empirical methods
(iii) Examination of the reaction kinetics

The parameters considered in these methods have a great variation in the measurement of the width of oxidation edges under the microscope in the measurements of luminescense and heat of wetting in methanol and water. Principally, the following parameters have been used to indicate the intrinsic reactivity of coal;

(a) Change of weight by oxidation
(b) Heat evolution

Table 1 Critical factors contributing to spontaneous combustion of coal.

INTRINSIC FACTORS	EXTRINSIC FACTORS	
Coal Properties	Geological Features	Mining Practice
1 Rank of coal 2 Moisture content 3 Pyrite content 4 Friability 5 Exinite and Vitrinite reflectance 6 Effective surface area of the reacting coal 7 Chemical constituents and mineral matter of coal 8 Permeability and diffusivity of coal to gases 9 Thermal conductivity and diffusivity of coal	1 Presence of faults in coal seams 2 Weak and disturbed strata cond. (weak natural roof and floor) 3 Thick seams containing bands of inferior coal 4 Depth 5 Multi-seams in close proximity	1 High losses of coal 2 Leaving coal roof and floor 3 Excessive fissuration due to strata movement 4 Caving to surface under shallow overburden or near outcrop 5 Thick seams * worked as component seams * worked in simultaneous lifts 6 Main roads 7 Pillars, ribsides and old workings 8 Coal heads and gob scouring 9 Quality of work 10 Old districts 11 Ventilation anomalies, imbalances, constrictions, large pressure differentials 12 Scope of leakages of air within goaf 13 Duration 14 Stowing

(c) Oxygen consumption
(d) Gaseous reaction products
(e) Changing conditions caused by oxidation
(f) Measurement of the rate of oxidation by means of chemical reactants
(g) Relative ignition points of coals
(h) Concentration of bound oxygen
(i) Humic acid production
(j) Oxygen, hydrogen, nitrogen, carbon content ratios

2.2 Practical Methods

One of the practical methods of managing the risk of spontaneous combustion during mining, transport and utilization of coal is to classify coal according to its degree of susceptibility to self heating and then take appropriate precautions with high risk coal. Various risk indices used in the past are as follows.

2.2.1 Incubation period method

The most practical method of classifying coal seams according to a spontaneous combustion risk index is the concept of 'incubation period'. The incubation period is usually defined as the time elapsed between the start of coal winding operations in a panel and the first sign of recognised heating. For low rank coals, the incubation period usually varies between 3 to 6 months and for high rank coals the period is found to vary between 9 to 18 months.

Spontaneous combustion risk can be quantified in terms of incubation period as shown in Table 2. For example, a coal seam which has an incubation period of less than 3 months presents a very difficult mining problem and consequently, poses a very high risk to spontaneous combustion.

Table 2 Incubation period risk index

Incubation period (months)	Seam classification
0 - 3	Very high risk
3 - 9	High risk
9 - 18	Medium risk
> 18	Low risk

As the method is based on past experience it can not be used for predicting the risk of spontaneous combustion in a virgin mining area.

Various other practical methods of classifying coal seam liable to heating are Olpinski method, Feng, Chakravorty and Cochrane Method (1973), Bystron and Urbanski method (1975) and Bannerji (1982). Descriptions of these methods are beyond the scope of this report.

For the purpose of this report, the laboratory methods have been classified as follows:-

(a) Laboratory methods which have been considered but are not in use in the UK.

(b) Current laboratory methods used in the UK.

2.3 Current Laboratory Methods NOT Used in the UK

These methods can be classified as follows:-

(i) Chemical method

(ii) Crossing-point temperature method

(iii) Ignition temperature methods

(iv) Different thermal analysis method

A brief description of these methods is included in appendix A1.

3 CURRENT LABORATORY METHODS USED IN THE UK FOR ASSESSING THE SUSCEPTIBILITY OF COALS TO SPONTANEOUS COMBUSTION

3.1 Static Isothermal Method (measurement of oxygen adsorption)

In this method, a series of bottles containing coal smaples are placed in a thermostat at a known temperature (around 30 C), then, the bottles are removed at certain intervals from the thermostat. Gases obtained from bottles are analysed and oxygen adsorption is calculated per g of coal (Elder et al 1945). It was concluded that if the volume of adsorbed oxygen after 96 hours at 30 C exceeded 300 ml/10 g coal, the coal is very liable to spontaneous combustion. If it is less than 200 ml, the liability of coal to spontaneous combustion is thought to be unlikely (Winmill 1915).

3.2 Dynamic Isothermal Method

The coal sample is exposed to a measured rate of oxygen or air flow and the disappearance of oxygen is measured by gas analysis. The volumetric values of the adsorbed oxygen are plotted against time then used as the measure of the rate and extent of the oxidation reaction. The procedure of measuring the oxygen adsorption may be updated due to improving technology and oxygen adsorption can be measured manometrically, volumetrically or by gas analysis (Guney and Hodges 1968, Carpenter and Giddings 1964). In the past, this method has been extensively used to verify the magnitude of oxygen adsorption by coals which in turn provides an opportunity for the assessment of spontaneous combustion risk, because, the higher the adsorption, the higher the heat generated.

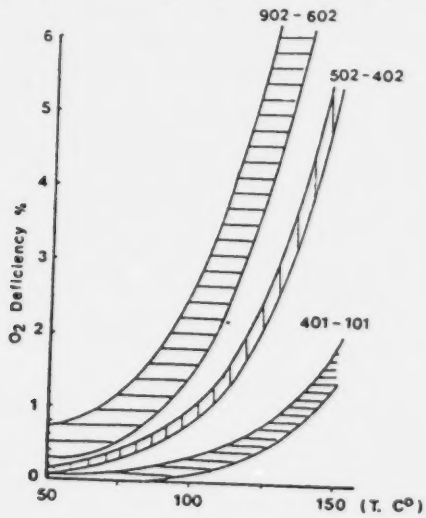

Figure 1 Oxidation of different rank coals (oxygen deficiency V temperature)
(after Chamberlain & Hall 1973)

The coal sample is placed in a thermostat and a stream of air passed through the sample while temperature of the thermostat is raised (normally 35 C per hour) steadily. The exit gases are analysed and oxygen deficiency percentage is plotted against coal temperature between 50 - 150 C as shown in Figure 1. Results were classified into three groups (Chamberlain and Hall 1973) and the ranks 602 and 902 (NCB classification) were defined to be the most reactive group.

3.3 Adiabatic Oxidation Method

Among the many methods for studying the self-heating of coal, the adiabatic oxidation test method is the most direct laboratory-scale technique (Davis and Byrne 1925, Cudmore 1964, Guney 1969, Shonhardt 1984). This method basically consists of passing a stream of air (or oxygen, nitrogen) through a coal sample placed in a thermostat cabinet which can be raised and controlled in temperature and observing the oxidation process in respect to the chosen parameter. Heat transfer to or from coal under test is virtually eliminated. The merits of this technique are discussed in detail in a subsequent section.

4 AN OPINION AS TO THE BEST METHOD

4.1 Direct Observation Method

A controlled environment on an experimental site is not suitable for risk classification for the following reasons:-

- Various environmental factors within the perimeter of the experimental site are difficult to control
- The experiment can turn into a great disaster in mines unless the test is controlled carefully
- Some factors may adversely effect the speed and overall cost of the experiment

4.2 Incubation Period Method

This method is a very valuable method for operating mining coal seams where previous mining experience exists. However, the technique cannot be applied to a new mining prospect where no previous mining has been carried out. Further, the method cannot be used to extrapolate the risk of spontaneous combustion in the same deeper seams where geologocal environment changes dramatically.

4.3 Laboratory Techniques

The type of laboratory test used to study the spontaneous combustion process would depend upon the information required because each test is suited to study a particular aspect of the process.

4.3.1 The CHEMICAL METHODS are based either on the measurement of the rate of oxidation or changes in chemical constitution coal or by investigating the hydro-aromatic structure or coal.

Thus, the chemical methods either need very specialized knowledge of coal structures or coal reaction chemistry. The hydrogen peroxide method can give an index of susceptibility of coal to spontaneous combustion , but the results could be misleading because the catalystic decomposition of hydrogen peroxide may result in heat evolution.

4.3.2 The CROSSING POINT TEMPERATURE METHOD of determining the proness of coal to auto-oxidation suffers from the following disadvantages:-

- Conditions of experiments such as rate of flow of oxygen, rate of heating, particle size of coal etc have to be meticulously maintained.
- Any minute change in the standardized test conditions can introduce large errors in the measurement of crossing-point temperature.
- Method is time consuming.
- The method utilizes temperatures much higher than those which prevail in underground mining operations, and therefore does not give any indication on the onset of self-heating of coal.

4.3.3 The ignition temperature method of classifying the self-heating potential of coal is based on the premise that a coal with the lowest ignition point and shortest time to ignition will obviously be more liable to spontaneous heating. This method again utilizes temperatures which are far above the temperatures encountered in coal mining environments and results are difficult to correlate to actual occurences in practice.

4.3.4 In the isothermal method the susceptibility of coal to spontaneous combustion is established from the rate of oxygen consumption. This method is particulrly suited to studying the effect of coal particle size, oxygen partial pressure, temperature and flow rates, on the rate of oxidation at selected temperatures.

4.3.4 The adiabatic method is suited to simulate the conditions closely resembling the mine environment or in a stockpile under which spontaneous combustion is likely to occur. Thermal conductivities

in a large mass of coal are very poor and therefore adiabatic methods, in which heat transfer to or from coal under test is virtually eliminated, represents more realistic test conditions. This method is useful in determining the following parameters.

- The self-heating rate of coal as opposed to the rate of heat production by isothermal methods.
- Investigating the effect of rank, petrography, chemical compostion and of inhibitions upon self-heating.
- It can be used to study the effect of moisture content of coal and that of ventilation current on spontaneous combustion.
- It can also be used to study the gaseous product on an extended range of temperatures.
- The test conditions simulte situations in goaf or waste heaps where circulation provides the necessary oxygen to oxidize coal but insufficient to dissipate the heat generated.

Therefore, the adiabatic method is the most favoured laboratory method for the assessment of spontaneous combustion potential of coal.

5 METHODS CURRENTLY USED BY THE OPERATORS

(a) British Coal is the major coal operator in the UK which has a wealth of underground coal mining experience. All coal seams have been classified into various risk categories based on the incubation period method and a list of seams liable to heating is maintained in each Area Office. When a coal mine is planned in a new coal seam, the physical, chemical properties of coal and rank are determined in the laboratory and these are correlated with the spontaneous combustion risk potential.

(b) British Coal's Regional Laboratories have the following test facilities which are used whenever required:-

- Static isothermal method
- Dynamic isothermal method

(c) The Central Electricity Generating Board (CEGB) is the major coal user in the UK. They do not have any test facilities to classify coal but they have comprehensive monitoring programmes of large coal stockpiles.

(d) Adiabatic test apparatus is available at various labortories which can evaluate coals liable to spontaneous combustion on contract basis. The clients of these test facilities are major coal mining developers (Shell Coal, British Petroleum) etc evaluating coal prospects in Africa, Australia, New Zealand etc or various shipping companies involved with coal cargo.

6 OPINION REGARDING THE MERITS OF THESE METHODS

The adibatic oxidation method presents one of the best techniques of evaluating the risk of spontaneous combustion of coal based on the intrinsic factors. They can also highlight the effect or moisture on spontaneous combustion. However, these methods have two major but surmountable limitations:-

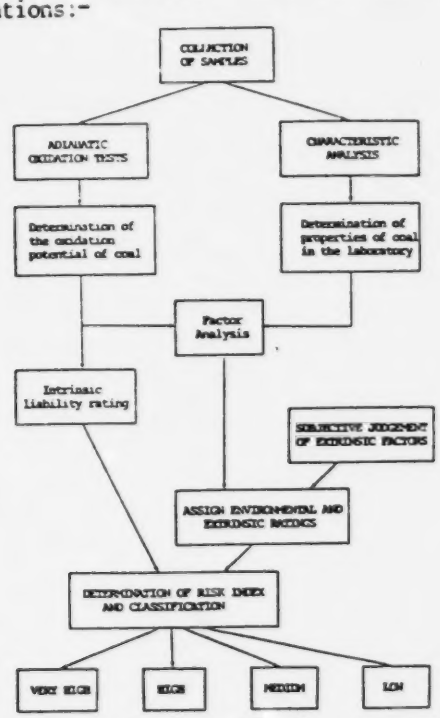

Figure 2 Schematic representation of the spontaneous combustion risk classification

- The test is time consuming. It takes 24 - 36 hours to acclimatize the test apparatus and 8 hours for the test. Thus 6 working days are required to complete one set of tests. This difficulty can be resolved by using a battery of calorimeters and automatizing the test procedure by incorporating computer control and monitoring techniques.

- This method does not take into account extrinsic factors which may promote the liability of coal to spontaneous combustion.

A technique based on the combination of adiabatic oxidation test, coal characterization analyses and subjective judgement has been recently used in the UK (Singh 1986, Singh, Demirbilek and Aziz 1985, Singh Demirbilek and Turney 1983).

A schematic diagram of this technique is presented in figure 2.

The oxidation behaviours of various coals were, therefore, tested under controlled adiabatic conditions in a specially designed adiabatic apparatus. The risk classification approach is based on the following discrete steps;

(i) Collect representative samples of coal from the coal seams.

(ii) Conduct adiabatic oxidation test on 100 g samples under controlled laboratory conditions and obtain temperature/time relationships at standard temperature, humidity, particle size and air flow conditions.

(iii) Classify temperature/time characteristics of various coals into four risk categories by correlating the laboratory result with the field instances of spontaneous combustion.

The oxidation results are supplemented with the available information regarding the chemical and the structural properties of coal seams and the effect of extrinsic factors promoting self-heating.

COMMENTS OF SAMPLE SIZE, HUMIDITY AND OTHER RELEVANT POINTS:-

The coal samples for the spontaneous combustion tests should be representative of the coal seam.

- The sample can be either a channel sample or a borehole sample.

- Immediate roof and floor of the coal seam, different layers of coal seam and dirt bands should be separately sampled. Both individual sample and composite samples should be analysed separately.

- A sample should be reduced to 1 kg size by standard techniques.

- Immediately after obtaining the sample, it should be flushed with nitrogen to exclude oxygen, and wrapped in silver foil and a leak-proof bag.

- The test is conducted on 100 g samples of coal (-210 microns), at a predetermined temperature of 40 C and the rate of change of temperature with time is observed at various humidity conditions as follows:-

  (i) In-situ moisture conditions of coal/saturated air
  (ii) Vacuum dry coal/saturated air
  (iii) Vacuum dry coal/dry air

The initial rate of heating and total temperature rise of vacuum dry coal/saturated air tests conditions form the basis for developing a risk classification system. The existence of dry coal underground and it's chance to get into contact with moist air could seem remote. However, this remoteness brings the safety factor automatically into the risk classification system.

APPENDIX 1

Chemical Methods

In these methods, small samples are treated with aqueous solutions of chemical oxidising agents. The experimental conditions differ greatly from atmospheric oxidation. So that, interpretation of the results is difficult. However, they have been considered to be useful for the investigation of the structure of coal.

The Wiesolowski method (Chamberlain and Hall 1973) briefly consists of heating 0.1 g of coal mixed with 0.05 g of sodium nitrite and subsequently 0.1 g of coal preoxidised by hydrogen peroxide and reduced by benzidene till they explode. The difference of explosion temperatures (dT) of the two samples was suggested to be an index of self-ignitability.

The change of "permanganate number" during oxidation has been suggested as a measure of the degree of oxidation of coals. The number represents the cubic centimeters of (N) potassium permanganate solution reduced by 0.5 g (dry ash free basis) pyridine-extracted coal in 1 hour at 100 C (Acherjee 1971).

The determination and measurement of the content of proxygen bodies formed during the oxidation reaction was thought to be a useful measure to predict the extent of oxidation of coals (Chalishazar and Spooner 1956).

Hurby (Cerny et al 1970) determined the combustion point with an initial contant temperature of 165°C together with a flow of oxygen and expressed the "relative oxidation degree" as follows;

$$O_s = \frac{T_2 act - T_2 ox}{T_2 act} \times 100$$

where T_2 act = the combustion point of coal in an active 1% aniline solution

T_2 ox = the combustion point of coal in a 1% oxidant hydrogen peroxide solution

Eastern European investigators have been more involved in chemical methods and since the 1960s their work has concentrated on the measurement of the decomposition of coal in hydrogen peroxide under adiabatic conditions (Lason 1959, Maciejasz 1959). The procedure used by Maciejasz is as follows.

A 3 g sample of coal, crushed to a size consisting of less than 0.06 mm was moistened with 1.5 cm of distilled water and placed in a Dewar flask which is standing in a bath heated to 18 C. When temperature parity is reached, 9 cm of 20% hydrogen peroxide was added. The hydrogen peroxide and coal was mixed, a thermometer was placed in the plug closing the vessel and the temperature was raised. At first, the time-temperature curves are virtually horizontal (Figure 2.1). The shorter the length of this section, the more reactive the coal tested.

Lately, this method had been used in France (Pregermain 1976) where coal sample were crushed in a nitrogen atmosphere to -0.063 mm size. The sample then moistened with 5 cm distilled water and when it has cooled it is placed in the Dewar flask. 30 cm of 20% concentration hydrogen

peroxide was added and the time-temperature variation recorded.

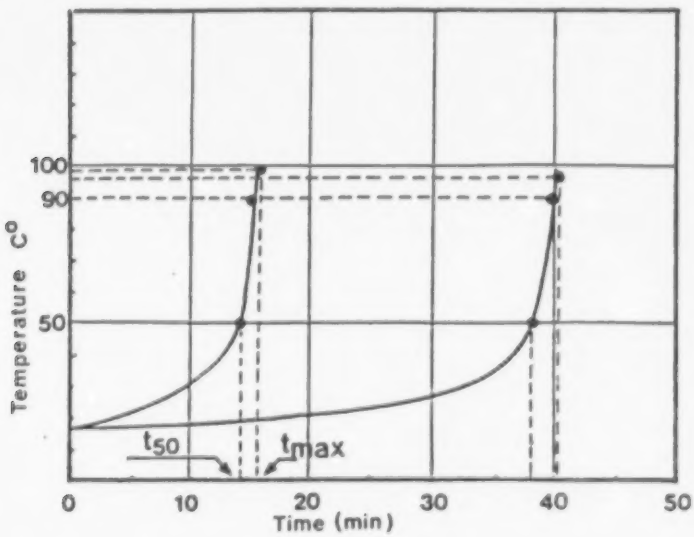

Figure 3 Typical time-temperature curves obtained by Maciejasz (after Pregarmain)

For practical purposes, the initial absolute temperature is taken to have no effect on the reaction. The time t, taken for the temperature to increase by 65 C (dT) is measured (eg 90 C if the initial temperature is 25 C). The index I is then obtained by the following formula;

$$I = \frac{100}{t}$$

Where, t is expressed in minutes. The shorter the reaction time, the higher the index. An I, greater than 16 signifies potentially severe spontaneous combustion problems. However, results could be misleading due to catalytic decomposition of hydrogen peroxide resulting in heat evolution.

APPENDIX 2

Crossing-point Temperature Method

In this method, the powdered coal sample is gradually heated in a suitable bath (Nandy 1972). Air or oxygen is passed through the coal at a prefixed rate and the particular temperature at which the coal bed temperature just crossed the bath temperature is defined as the crossing-point temperature of coal (Figure 4).

It has been suggested that coals with crossing-point temperatures from 120 C to 140 C may be considered to be highly susceptible to self-heating, coals having crossing-point temperatures between 140 - 160 C are moderately susceptible, whereas the poorly susceptible coals are likely to show rather high values such as 160 - 190 C or more.

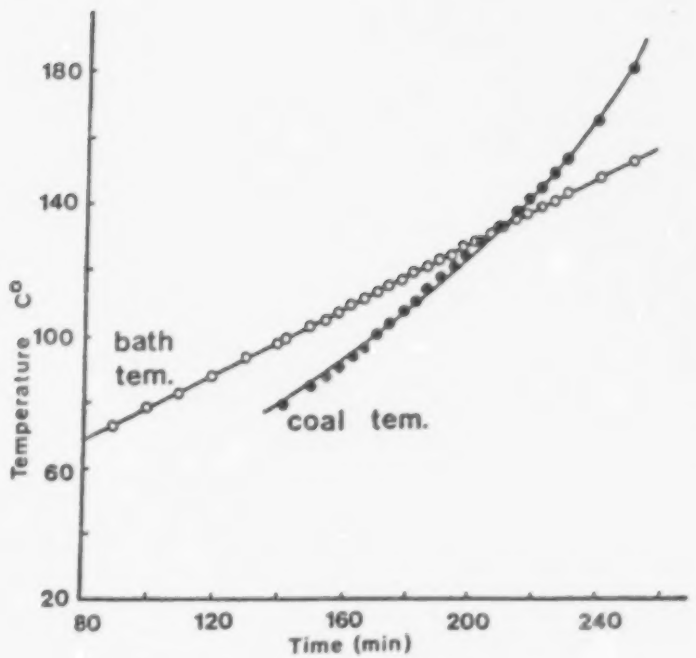

Figure 4 A typical crossing-point temperature result (after Banerjee et al 1972)

APPENDIX 3

Ignition Temperature Method

A coal bed which has an air or oxygen flow through itself, is slowly heated in a furnace or bath. Eventually, the coal and ambient temperature becomes momentarily equal, usually the coal temperature increases, fumes and ignition points range between 150 C to 500 C depending on conditions and rank of coal. The ignition temperature of a particular coal sample provides the minimum temperature necessary for the inflammation of coal. The time period elapsed until ignition refers to the oxidation rate. A coal which has the lowest ignition point and shortest time till ignition, will obviously be the most liable coal to spontaneous combustion (Acherjee 1971).

Differential Thermal Analysis Method

The technique consists of heating a small test specimen at a rate of 5 C/min and continuously recording the instantaneous temperature difference (dT) between it and a reference material (calcinated alumina) which is heated under almost identical conditons (Banerjee and Chakravorty 1967, Berkowitz 1957). The corresponding temperature of the inert reference material (T) is also noted in order to draw the resultant thermogram which is a record of (dT) versus (T) (Figure 5). The thermogram is explained in three stages. In the first, the temperature of coal decreases to a minimum (dT is negative) and then starts increasing which is defined to be the second stage. The third stage shows very steep rises in heat evolution. The study of the second stage was thought helpful for the understanding of the self-heating characteristics of coal.

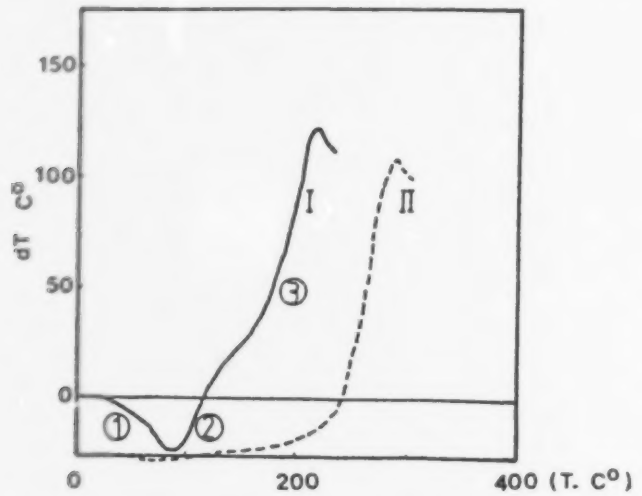

Figure 5 DTA Thermograms I - Highly susceptible to heating
II - Not very susceptible to heating
(after Banerjee & Chakravorty 1967)

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FEATURES

A PRACTICAL SYSTEM OF CLASSIFYING COAL SEAMS LIABLE TO SPONTANEOUS COMBUSTION

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Abstract

The paper outlines the risk of spontaneous combustion in modern longwall mining and identifies the importance of forward mine planning and design in preventing serious consequences of spontaneous heating. Current techniques of classifying coal seams according to their proneness to spontaneous combustion are briefly presented together with their limitations. Factors affecting liability of coal to spontaneous combustion depend upon both intrinsic factors as well as extrinsic factors promoting self-heating. A practical system of classifying coal seams according to spontaneous-combustion risk potential, based on adiabatic oxidation tests as well as the influence of extrinsic factors is presented. Some of the results of intrinsic reactivity tests on coals from different countries are presented together with the new developments in the calorimeter design.

Introduction

Coal mining historically has been associated with the fire hazards due to spontaneous combustion; consequently in the past considerable research efforts have been directed towards solving this problem. In spite of these efforts, in recent years incidences of spontaneous combustion of coal in underground mining, during storage in large stockpiles, and during seaborne transportation have considerably increased. In underground mining operations, the increased incidences of spontaneous combustion can be attributed to the modern intensive longwall mining methods associated with thick coal-seam extractions. As longwall faces are now equipped with very expensive face equipment (often exceeding $4 million) and the time lag between first detection of dangerous conditions is too short, it is not always possible to salvage face equipment safely in the event of fires. For example, in the UK at least 2-3 fully mechanised longwall faces are permanently lost every year due to uncontrolled spontaneous heating resulting in serious economical losses. Operational difficulties and consequencial financial losses due to sudden loss of a coal face cannot be easily quantified. The delay in providing an alternative production face may present considerable strains on the Colliery's financial resources and some marginal collieries may not ever recover their financial viability again. An approach to preventing this situation is to identify coal seams liable to heating and take adequate precautions during planning and design stages of mining so as to avoid sudden outbreak of fire.

The paper outlines a technique of assessing spontaneous-combustion risk index whether very high, high, medium, or low risks. Adequate planning and operational precautions for preventing spontaneous combustion should be taken in very high- and high-risk coal seams. Detailed considerations should be given to planning the ventilation system, the method of coal extraction to minimize coal losses, ground control including gateside pack design, the gas monitoring system, the salvage of the coal face, and the emergency organization dealing with spontaneous combustion. Similar precautionary measures are also necessary in planning safe storage and seaborne transportation of coal.

Spontaneous-combustion Risk Indices

A large number of factors influence the liability of coal to spontaneous combustion, but these can be grouped into two categories as follows:

a) Intrinsic factors based on the inherent characteristics of coal and beyond control of mine operators.
b) Extrinsic factors based on mining practice which can be controlled with forward planning and mine design.

Table 1 shows the critical factors contributing to spontaneous combustion of coal.

One of the well-established approaches for systematically dealing with the spontaneous-combustion problem is to classify coal seams

TABLE 1. Critical factors contributing to spontaneous combustion[1]

Coal properties	Mine environment	
	Geological features	Mining practices
1. Rank 2. High moisture 3. High pyrite 4. High friability	1. Presence of faults in coal seams 2. Weak and disturbed strata 3. Thick seams containing bands of inferior coal 4. Seams under shallow overburden 5. Multi-seams in close proximity	1. High losses of coal in worked-out area 2. Excessively fissured strata due to stress relief 3. Surface collapse under shallow overburden or near outcrop 4. Mining of thick seam by caving-partial extraction of seams 5. Ventilation anomalies, imbalances, constrictions, large pressure differential.
Intrinsic, Beyond Control		Extrinsic, can be controlled

according to their risk indices and to take suitable precautions in "high-risk" and "very high-risk" seams during mining, transport, and storage in order to prevent outbreaks of spontaneous combustion.[2]

Risk Indices

In the past, several attempts have been made to classify coal seams according to their risk index.

Incubation period method. The most practical method of classifying coal seams according to spontaneous-combustion risk index is the concept of "incubation period." The incubation period is usually defined as time elapsed between the start of coal-winning operations in a panel and the first sign of recognised heating. For low-rank coals, the incubation period varies between 3 to 6 months and for high-rank coals the period is found to vary between 9 to 18 months.

Spontaneous-combustion risk can be quantified in terms of incubation period as shown in Table 2. For example, a coal seam which has an incubation period less than 3 months presents a very difficult mining problem and, consequently, poses very high risk to spontaneous combustion. Table 2 also shows the relationship between risk classification, incubation period and assigned risk index (discussed in a subsequent section). As this method is based on past experience, it cannot be used for predicting the risk of spontaneous combustion in a virgin mining area.

Olpinski method. This method of classifying coal seams with regard to spontaneous heating is based on the experience in Polish mines. Olpinski[3] has taken into account both intrinsic and extrinsic factors to formulate a spontaneous-combustion risk index for coal as follows:

$$P = S_1 b + (S_1 + S_2 + S_3 + S_4 + S_5 + S_6 + S_7)$$

where

- P = probability of fire risk involved in the system
- $S_1 b$ = Spontaneous heating susceptibility of coal
- S_1 = Coal left in mines (worked-out areas)
- S_2 = System/method of working
- S_3 = Ventilation method
- S_4 = Scope of leakages of air (within the worked-out area)
- S_5 = Degree of wetness of coal seam
- S_6 = Depth of a given mine
- S_7 = Intensity/degree of ventilation

By assigning various values to the above factors, based on mining experience, the spontaneous-combustion risk of coal is estimated. If $P < 120$, the coal is considered to be safe, whereas $P > 120$ indicates the probability of spontaneous-combustion risk. This approach is mainly based on the local mining experience. It does not classify degree of risks and is not easily amendable to wider applications.

Feng, Chakravorty, and Cochrane technique. A similar approach by Feng, Chakravorty, and Cochrane[1] and Nandy[4] utilized a liability index based on relative ignition temperature and an environmental index based on coal loss, fissuration, and ventilation pressure differentials to formulate the following risk index:

$$\text{Liability index} = \frac{\text{Average heat rate between } 110^{\circ}\text{-}220^{\circ}\text{C}}{\text{Relative ignition temperature}} \times 1000$$

Ratings of liability and environmental indices were given by Feng.[1] The risk index is then computed as the product of liability index and environmental index:

$$\text{Risk index} = \text{Liability index} \times \text{Environmental index}$$

The coal liable to heating was assigned 3 ratings —low, medium, and high risk, with risk indices of (0-10), (10-20) and (20-40), respectively. Based on this system, Feng et al.[5] classified Canadian coals according to their degree of liability to spontaneous combustion. This technique, like the previous ones, has not received wider application because:

a) The crossing-point temperature method developed by Feng et al.[5] utilizes temperatures much higher than those which prevail in underground mining operations, and therefore, does not give any indication of the onset of self-heating of coal.
b) The assessment of environmental index is based on subjective judgments of factors affecting coal loss, degree of fissuration, and ventilation pressure difference and no detailed quantitative assessment of factors such as moisture content is attempted.

Bystron and Urbanski method. Bystron and Urbanski[3] devised a scheme for the assessment of spontaneous-combustion risk potential of coal in stockpiles. This scheme is based on assigning risk ratings to various factors as given in Table 3.

Both intrinsic as well as extrinsic factors are taken into account. The intrinsic factors are based on the rank of coal as well as ash content. The extrinsic factors taken into account are the stockpiling practices. By assigning various risk ratings the spontaneous-combustion risk potential is assessed as shown in Table 3. This method, which is basically subjective judgment, has found favour with some leading consultants in solving practical problems.

TABLE 2. Practical spontaneous-combustion risk index

Incubation period (months)	Assigned Risk Index	Seam classification
0 - 3	> 40	Very high risk
3 - 9	20 - 40	High risk
9 - 18	10 - 20	Medium risk
> 18	1 - 10	Low risk

TABLE 3. Ratings assigned by Bystron and Urbanski[3]

Factors		Ratings
Intrinsic factors	1. Coal rank	+1 to +8
	2. Grade of coal	0 to +7
	3. Ash content	0 to -2
Extrinsic factors	1. Surroundings	0 to +2
	2. Stockpile method	+8 to -25
	3. Mass of coal in stockpile	0 to +10
	4. Height of stockpile	-5 to +8
	5. Presence of device in the coal stockpile	0 to +6
	6. Period of storage	+10 to -1
	7. Method of monitoring	+5 to -10

TABLE 4. Spontaneous-combustion risk classification of coal seams

Risk Classes	Adiabatic test		Risk rating in Ad.test	Total risk rating	Incubation period (months)
	Initial rate of heating C°/hr	Total temp. rise C°			
Low risk	<0.6	<2.5	1	1 -10	>18
Medium risk	0.6-1.2	2.5-4.5	2	11-20	9-18
High risk	1.2-2.0	4.5-7.0	4	21-40	3-9
Very high risk	>2.0	>7.0	8	>40	0-3

Banerjee method. Banerjee[8] proposed a scheme for the appraisal of spontaneous-combustion risk index based on the examination of multiple contributory factors including both intrinsic as well as various mining parameters. The risk probability of spontaneous combustion for an individual mining condition depends upon inherent factors contributing to fire risk and the degree to which particular mining parameters affect these factors. The two types of parameters can be assigned ratings to facilitate the calculation of risk index by summing up all input ratings. This scheme is complicated and requires collection of large data in addition to a certain degree of subjective judgment.

Adiabatic oxidation method. Over the past two decades considerable research has been conducted at Nottingham University to determine the actual reactions responsible for spontaneous combustion in coal and to determine the degree of susceptibility of coal to spontaneous combustion by means of adiabatic oxidation tests. In concept, the test consists of the adiabatic oxidation of a 100-gram sample of coal (-210 microns) at a predetermined temperature, observing the rate of change of temperature with time under the following humidity conditions:

- —In-situ moisture conditions of coal/saturated air
- —Vacuum dry coal/saturated air
- —Vacuum dry coal/dry air

The criteria used for assessing the spontaneous-heating potential of coal are initial rate of heating, total temperature rise, pyrite content, volatile content, and international rank classification of coal. Although this technique gives an indication of self-heating potential of coal by examining the contribution made by the intrinsic factors only, the effect of change of moisture content, rate of flow of air, and ambient temperature can also be evaluated. Past experiences have shown that high-rank coals which are not intrinsically reactive, may under suitable circumstances, present "very high risk" during mining operations.[6]

This review also indicates that all classification systems are either based on past experience, laboratory intrinsic reactivity tests, subjective judgment, or a combination of intrinsic and extrinsic factors. It is therefore suggested that, in order to develop a practical classification system acceptable to practical engineers, the intrinsic reactivity test result should be supplemented with subjective judgment on extrinsic factors.

Development of a Practical Spontaneous-combustion Risk Index for Longwall Mining

An approach adopted by the author for the classification of coal seams liable to self-heating is based on the following discrete steps:

a) Collect representative samples from the coal seams of high- medium- and low-risk categories from the UK, India, Turkey, Australia, Botswana, South Africa, and USA.
b) Conduct adiabatic oxidation tests on 100-gram samples under controlled laboratory conditions and obtain temperature/time relationships at standard temperature, humidity, and air-flow conditions. All coals have been classified in the risk categories defined in Table 4.

Figure 1 shows the intrinsic risk classification based on adiabatic experiments. It should be emphasised that the classification is based on initial rate of heating, total temperature rise, proximate analysis, calorific value, rank classification, and pyritic sulphur content.

Total risk rating is estimated by the modified Bystron and Urbanski method[3] as modified by the Nottingham research team (Table 5).[7, 8]

The tests usually extend over a period of 8-12 hours. Temperature readings are determined by a thermoccuple and effluent gas samples are taken at quarterly-hour intervals. The gas samples are subsequently analysed to calculate CO/O_2 deficiency ratio to indicate the presence of spontaneous combustion. The results are expressed on a 100-gram dry-coal basis and the adiabatic temperature rise and fall with time due to self-heating of coal at various humidity conditions are recorded. The test condi-

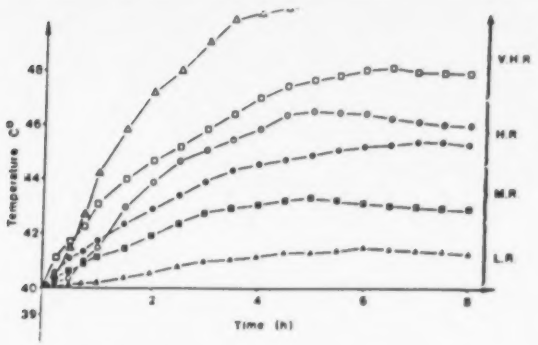
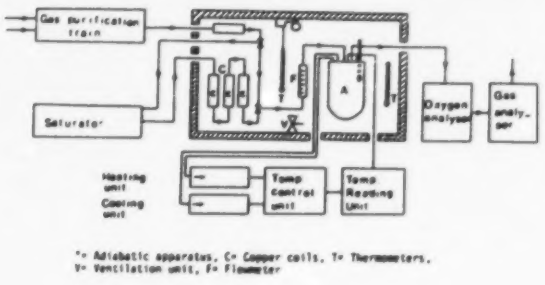


Figure 1. Spontaneous-combustion risk classification.



A= Adiabatic apparatus, C= Copper coils, T= Thermometers, V= Ventilation unit, F= Flowmeter

Figure 2. Flow diagram for experimental set-up for adiabatic oxidation test.

TABLE 5. Modified spontaneous-combustion risk classification for longwall mining[a,b,c]

Factor Nos.	Factor classification	Factor Rating
INTRINSIC FACTORS	COAL GROUP 1- Low susceptibility index In. rate of heating < 0.6°C/hr and Total temperature rise 0-2.5°C	+ 1
	COAL GROUP 2- Medium susceptibility In. rate of heating 0.6-1.2°C/hr Total temperature rise 2.5-4.5°C	+ 2
	COAL GROUP 3- High susceptibility In. rate of heating 1.2-2°C/hr Total temperature rise 4.5-7°C	+ 4
	COAL GROUP 4- Very high susceptibility In. rate of heating > 2°C Total temperature rise > 7°C	+ 8
EXTRINSIC FACTORS	Grades of coal	
	Fines	0
	Thin coal left on roof	+ 2
	Thick coal left in roof	+ 5
	Ash content %	
	< 20	0
	21-30	- 1
	> 30	- 2
	Waste support method	
	Caved waste	0
	Hang-up waste	+ 4
	Mining method	
	Longwall mining with conventional packing	+ 8
	Longwall advance, pump packing (for poor floor add +3)	+ 4
	Longwall retreat	+ 1
	Longwall retreat, bleeder roads	+ 8
	Seam recovery	
	Total seam extraction	0
	0.3-0.5 m roof coal left	+ 5
	>0.5 m roof coal left	+ 8
	Seam thickness	
	<1.5 m	- 1
	1.5-3.0 m	+ 2
	>3.0 m	+ 3
	Thick seam slicing method	+ 8
	Ventilation method	
	Conventional	0
	Return gate fan and duct for methane control	+ 4
	Daily advance	
	<1.0 m	+ 5
	1.5-2.5 m	+ 2
	>2.5 m	0
	Monitoring	
	No monitoring	+ 5
	Routine monitoring	- 2
	Continuous monitoring	- 7

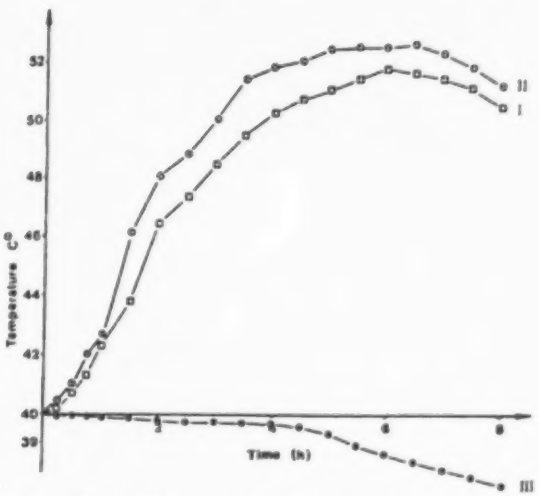


Figure 3. Typical adiabatic test results on Maamba coals.

tions are standardized as coal with in-situ moisture/saturated air, vacuum dry coal/saturated air, and vacuum dry coal/dry air. All tests are conducted at airflow of 200cc/min.

Figure 2 shows the experimental set-up for adiabatic oxidation tests. Figure 3 shows the test results for a coal sample from Maamba Colliery, Zambia, for the above test conditions. Curve III illustrates normal oxidation of coal under dry conditions indicating a small amount of heat produced. This appears to indicate that oxidation alone does not sufficiently increase the temperature of coal to create a heating problem. Curve II indicates the oxidation of coal and the simultaneous absorption of water vapour. The heat generated by this phenomenon may increase the coal temperature considerably giving rise to serious heating. Curve I indicates the oxidation of in-situ-moisture coal in the presence of saturated air giving an intermediate heat-rise condition.

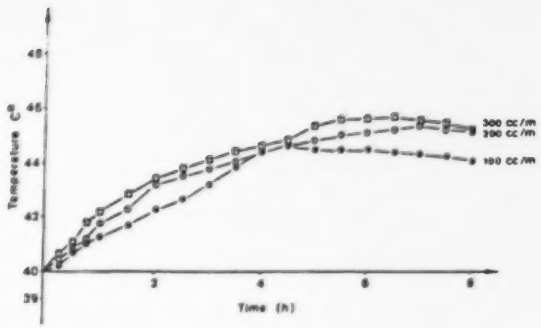


Figure 4. Effect of variation of air-flow rate on rate of temperature rise.

TABLE 6. Classified adiabatic oxidation results

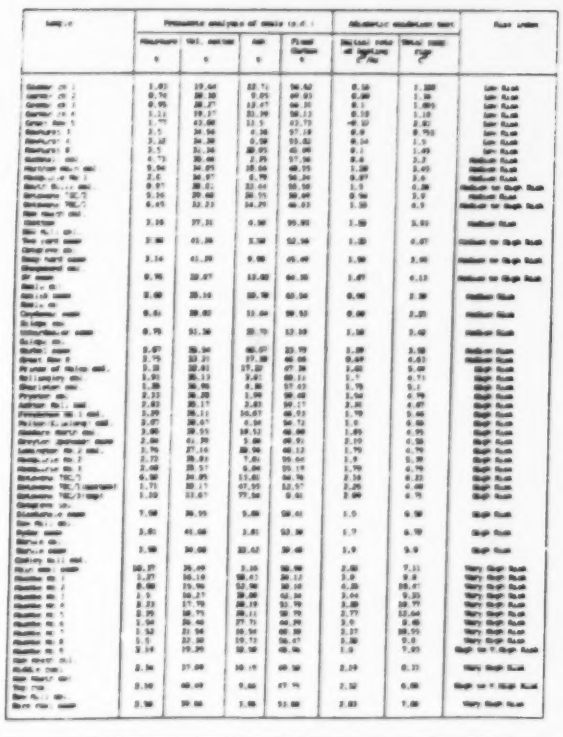


Figure 4 shows the effect of variation of air-flow rate on the rate of temperature rise in an adiabatic oxidation test. The results indicate that for a given coal type there is an optimum flow rate at which temperature rise is maximum. Table 6 illustrates the classified results obtained throughout this project. Some of the tests conducted under dry-air conditions show a cooling-type temperature-time curve. This indicates a test condition where the heat generated by the adiabatic oxidation reaction is smaller than the heat absorbed by evaporation of moisture in the coal plus the heat dissipated by the air current. This condition indicates that by controlling the mine environment, it is possible to control the risk of spontaneous combustion on this type of coal.

Further Developments

The adiabatic oxidation test is time consuming and labour intensive, as a set of three experiments takes at least 6 working days to complete. Moreover, the temperature-control unit has a certain amount of built-in time lag to control the calorimeter's external temperature. Both of the above limitations can be overcome by using several microprocessor-controlled calorimeters in parallel. A research project concerned with the development of a microprocessor-controlled adiabatic calorimeter has been initiated at Nottingham University.[9] It contains a vacuum circuit for drying coal, a nitrogen circuit for acclimatising coal, a dry air circuit for testing, and saturate air circuits. A servo flow valve electronically controls the flow rate of air or nitrogen making continuous monitoring and control of the adiabatic experiment possible.

Conclusions

A practical approach to the planning of mining operations in coal seams liable to spontaneous combustion is to classify coal according to its susceptibility to self-heating. Special precautions must be taken in very high- and high-risk seams during development, coal extraction, and subsequent transport, and the storage and utilization of coal in order to prevent the outbreak of spontaneous heating. A system of assessment of coal for spontaneous-combustion risk based on adiabatic oxidation tests is described. This system of classification offers a most practical way of identifying the degree of risk in coal to self-heating, and therefore enables advance precautionary measures to prevent outbreak of spontaneous combustion.

Acknowledgments

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APPENDIX D

Information on Methods of Testing Coal Susceptibility to Spontaneous Combustion as Applied in East-European Countries

by

Jerzy Muzyczuk and Barbara Trzebicka

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INFORMATION

on Methods of Testing Coal Susceptibility to Spontaneous Combustion as Applied in East-European Countries.

In East-European countries there are used different methods of testing coal to determine its susceptibility to spontaneous combustion. Most frequently those tests are performed under the "coal-air" system and less - under systems of "coal-oxygen" or "coal - oxidizing water solution".

Depending on the method of tests applied there are analyzed various oxidation effects, namely:

- the increase of coal temperature
- the consumption of oxygen or other oxidizing agent
- the emission of gassy products of reaction, especially carbon monoxide and dioxide
- the producing of non-gassy products of reaction, such as humic acids or functional oxygen groups in superficial compounds.

There are applied various techniques of testing in which the coal undergoes oxidation in the following conditions:

- isothermal,
- quasi-adiabatic,
- with forced growth of temperature, most often, as a determined constant rate.

The following are taken as the criterions for determining the susceptibility to spontaneous combustion:

- the quantity of consumed mass of oxygen, or other osidizing agent, per unitary mass of coal and/or the reaction products obtained in a determined test interval.
- the rate of oxidizing and or yielding reaction products, instantaneous or average for a determined test interval, with reference to a unitary coal mass.
- the properly defined temperature of initiating or considerable speeding-up of the oxidizing reaction, among others, the so called ignition temperature.
- the rate of temperature growth under specifically determined oxidation conditions.

An optimal approach to the question of spontaneous combustion tests of coal cannot be determined unequivocally since it depends on the purpose to be served by the tests. For complexity of the processes leading to spontaneous combustion of coal, as conditioned by different factors determining the condition of the sample under testing, as well as for the external conditions, it is necessary to perform complex tests. It is worthwhile to pay especial attention to tests performed under quasi-adiabatic conditions, which render simulatation of a coal self-heating process in a laboratory scale. Nevertheless, the basic information necessary for working but prognoses of the process run, can be obtained on the basis of isothermal tests performed under different temperatures and over a sufficiently long time interval.

Apart from isothermal and quasi-adiabatic methods of testing coal to determine the oxidizing and self-heating process there have been developed in Poland other methods suitable for determining in bulk the appropriately defined spontaneous combustion index of coal.

One of those methods is the Olpiński's method in which one determines, for an adiabatic point, the rate of growth of temperature of a 0.3 g coal pellet introduced in an air stream having the temperature of 237°C.

On the basis of that index and with taking into account the ash content of the coal sample tested there has been worked out a classification system by which coals are divided into 4 groups of differing spontaneous combustion nature. That method is included in an industrial standard specification and it has been widely applied in practice since the 1950's.

Another one of those methods, developed in the recent years and applied in research work, is a method of determining the reaction rate for a suitably prepared coal sample of 0.5 g mass treated with an alkaline water solution of potassium permanganate in the room temperature. The reaction rate is determined as the mean value for the first hour of oxidation. The results of tests made according to this method are correlated with test results obtained by the Olpiński's method.

In the fire prevention practice the mine ventilation service units take into account the results of tests of spontaneous combustion of coal made with the Olpiński's method.

The Olpiński's method has been also adapted for spontaneous combustion tests of coal in Czechoslovakia and Jugoslavia. In the USSR instead, as is known from literature there are used two methods: MakNII and IGD.

In the MakNII method a 100 g coal sample of 0.3 - 0.43 mm grain size undergoes heating in an air stream at a rate of 25 K/min and for temperature intervals, e.g. 150 - 200°C or 125 - 175°C, depending on the degree carbonification and origin of coal sample/type of coalfield/one determines the appropriately defined index with taking into consideration the mass of oxygen consumed and gas components produced /CO_2 and CO/.

In the IGD method a 100 g coal sample of 1 - 3 mm grain size undergoes oxidation with air in a closed tank from which, at certain time intervals, air samples are taken for an analysis and the negative pressure produced is eliminated by letting some fresh air in. The oxidation process runs at a temperature of 25°C. On the basis of test results one determines the mean value of a constant reaction rate determined for the time interval of 50 - 250 h.

The spontaneous combustion index determined by the Olpiński's method properly represents the spontaneous combustion nature of coal and in a long-time practice in Poland it has proved successful both in working out fire hazard prognoses and for determining guidelines for fire prevention in the processes of mining, storage and transportation of coal.

Doc.dr. Jerzy Muzyczuk
dr. Barbara Trzebicka

Katowice, Nov. 28, 1986

SUPPLEMENTARY INFORMATION /2/

on coal spontaneous combustion tests applied in East-European Countries.

To make the information of Nov. 6, 1987 complete presented hereby are broader descriptions of the methods of determining the susceptibility of coal to spontaneous combustion, the Soviet IGD and Mak NII methods and the Polish one of Olpinski. Also added are brief comments and a reference list /1 ÷ 6/ for those interested in more details.

A. The IGD Method /5/

In this method a coal sample of 100 g mass and 1 ÷ 3 mm grain size undergoes oxidation with humid air of 25°C temperature for 250 hours. For this purpose the sample is placed in a sorption glass container of 60 mm dia. and 600 cm^3 capacity, over a water layer ensuring a constant vapour pressure. The container is provided with 2 stub pipes /the inlet and outlet one/ which enable the sampling of air for chemical analysis and the scavenging with fresh air after each sampling.

Air samples are taken every 24 h over the time period from T' = 50 h to T" = 250 h, counted from the beginning of the test.

For successive equal time intervals $\triangle T_1$ = 50 ÷ 74 h $\triangle T_2$ = 74 ÷ 98 h, ... $\triangle T_n$ = 226 ÷ 250 h the constant oxidation rate U_i can be determined by applying the formula as follows:

$$U_i = \frac{V}{N \, \Delta T_i} \ln \frac{C_o \, /1 - C_a/}{C_a \, /1 - C_o/} \qquad /1/$$

where:

V	-	volume of air in the sorption container, cm^3,
N	-	mass of coal sample, g,
ΔT_i	-	oxidation time / ΔT_i = 24 h/, h,
C_o, C_a	-	initial /C_o/ and terminal oxygen concentration

$$\left[U_i\right] = \frac{cm^3}{g \cdot h}$$

On the basis of the value of U_i one can determine the mean value of U_{25} for the whole test period by applying the formula:

$$U_{25} = \frac{\sum_{i=1}^{n} U_i^{\circ}}{n} \qquad /2/$$

where: $i = 1, 2, 3, \ldots\ldots n.$

Though the above method is not applied in Poland in its version as described here, we can, however discuss its advantages which, in our opinion, are as follows:

The Advantages of the IDG Method

1. A rational manner of defining the U_{25} index as a mean value of constant oxidation rate under conventional conditions of tests.
2. A relatively simple apparatus set.

The Disadvantages of the IDG Method

1. A long test cycle, lasting 250 h.

2. A considerable influence of the coal sample history on the result of test. In this connection there arises a necessity of observing severe restrictions concerning the sampling and the transportation and storage of samples.
3. The formula /1/ does not take into account the influence of methane emitted from coal on the oxygen concentration C_a.

B. The Mak NII Method /4, 5/

In this method a coal sample of 100 g mass of 0.30 ÷ 0.43 mm grain size undergoes oxidation with a humid air stream /90 ÷ 95% at the inlet/ of a constant rate of 10 1/h under the condition of a forced temperature growth. For this purpose the sample is placed in a cylindrical copper vessel, of 40 mm inner dia. and 180 mm height, provided with an air inlet stub pipe and an outlet stub pipe /for taking the oxidation products/. The vessel is immersed in an oil bath which is heated from 25°C to 250°C at a rate of 25°C/h.

The susceptibility of coal to spontaneous combustion is determined on the basis of the results of analyses made on samples of air, running out of the reaction vessel, taken at equal time intervals corresponding to coal temperatures of 75, 100, 125, 150, 175 and 200°C. For the said samples the following features are subject to determination: the contents of oxygen, carbon dioxide and carbon monoxide.

It has been accepted in this method to use for determining the susceptibility of coal to spontaneous combustion an index S defined by the formula

/3/

$$S = \int_{t_n}^{t_k} f_1(t) \sqrt{[f_2(t)]^2 + [f_3(t)]^2}\, dt$$

where:

$f_1/t/$, f_2/t and $f_3/t/$ - indices of oxygen loss $/f_1/$, carbon dioxide content increase $/f_2/$ and carbon monoxide content increase $/f_3/$determined as functions of temperature t of exponential type:

$$f_i = a_i e^{b_i t} \qquad /i = 1, 2, 3/ \qquad /4/$$

Depending on the origin of the coal sample/type of the coalfield/ and the degree of metamorphism of coal /its type/ different temperatures $/t_n$, $t_k/$are taken as the limits of an integral determined by the formula /3/.

In extreme cases they correspond to the temperature intervals of /80°C, 100°C/ and 150°C, 200°C/.

Comments on the Mak NII Method

That method is not used in Poland and for that reason the authors of this work do not feel competent to discuss its advantages and disadvantages. Reservations may be raised due to a complicated, artificial and ambiguous manner of defining the index S and to the usage of an incomplete analysis of the oxidation products for determing the f_1, f_2 and f_3 indices. A drawback in this method is also a relatively long test cycle determined by the rate of heating coal, 25°C/h, and the maximum temperature of 250°C.

C. The Olpinski's Method

In this method, for spontaneous combustions tests there is used a coal sample of 0.06 - 0.075 mm grain size obtained by way of manifold disintegration and screening. By using a press and a mould of a suitable design one should make a pellet of 0.3 g mass and cylindrical form with a pit enabling its setting on the tip of a thermoelement used for measuring the temperature in the process of oxidation effected by air.

The pellet is made under strictly determined conditions of load acting, over a time interval of /20 $\pm$ 1/ S and with a force of 2270 N, on the mould mandrel /piston/ under which the required quantity of coal sample must be introduced. The required sample mass is determined on the basis of successive observations of the longitudinal section of the pellet in such a manner that the thickness of the wall at the point of its contact with the thermoelement tip be equal to /1 $\pm$ 0.2/ mm.

Thus prepared coal pellet is to be put on a slightly curved tip of a thin-walled glass cover of the thermoelement and, together with the latter, it should be introduced in a reaction tube of 24 mm I.D. through which hot air /237°C/ is passed at a rate of /10 $\pm$ 2/ cm^3/s. Owing to a thermostat system the central part of the reaction tube has the same temperature. The thermoelement cover is mounted on a ground plug which closes the reaction tube outlet, after the pellet has been put inside while the oxidation products escape through a side stub pipe and are delivered to a ventilation duct.

The thermoelement, whose cool ends are integrated with a thermostat system to keep a constant reference temperature /t_o = 20C/, is connected to a millivoltmeter monitoring the run of temperature of the pellet during the test cycle, i.e. from the room temperature /the initial temperature of the pellet/to the moment of exceeding 350°C when the recorder gets switched off.

It is accepted to determine the spontaneous combustion nature of coal by the rate of growth of temperature of the pellet at the adiabatic point corresponding to the temperature of the reaction tube interior and the air passing through it.

The spontaneous combustion index of coal is defined by the formula:

$$Sz^a = \lim \frac{dt}{dT}$$

$$/t = t_a/$$

where:

t - temperature of coal pellet, °C,
t_a - temperature of reaction tube interior /t_a = 273°C/,
T - time, min.

The index is determined as the value of the coefficient of slope of a tangent to the temperature /t/ curve represented as a function of time T.
A criterion of the coal classification developed in Poland and based on spontaneous combustion nature an index Sz^{af} has been accepted, which is determined by a formula:

$$Sz^{af} = \frac{100\ Sz^{a}}{100 - A^{a}} \qquad /6/$$

where: A^a - ash content, % by weight.

The Advantages of the Olpinski's Method

1. A relatively simple apparatus set /no analysis of oxidation product contents is necessary/,
2. Rational and proper, from a practical point of view, manner of defining the coal spontaneous combustion index,
3. A short test cycle of 3 to 5 min.

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APPENDIX E

Report on Visit to European Laboratories

APPENDIX E

Report on Visit to European Laboratories

1. INTRODUCTION

Following the initial literature review and associated communications, it became evident that work was being carried out in both France and the Netherlands that appeared particularly relevant to the study. Consequently, an amendment was issued to the contract to visit the CERCHAR Laboratories at Vernuil-en-Hallatte, France and the Prins Maurits Laboratory at Rijswijck, the Netherlands. This Appendix outlines the findings of these visits.

2. CHERCAR

2.1 Background

The visit took place on March 2 and 3, 1987.

The Centre d'Etudes et Recherches de Charbonnages de France (CHERCHAR) has been the research arm of the french coal industry for 80 years. It now serves many related industries in the area of industrial safety in hazardous environments.

It has an ongoing program into spontaneous combustion of coal in mines, during storage and as pulverized fuel.

Discussions were held with:

Clause Froger, Conseiller du Directeur de Recherches
Simon Pregermain, Ingenieur au Groupe Chimie du Carbon
Douglas Carons, Ingenieur au Groupe Chimie du Carbon

The explanation of the work carried out by CERCHAR described below gives an insight into their priorities and the problems of the french coal industry.

The major cause of spontaneous combustion is generally assigned to oxidation of coal, but this exothermic reaction is not always sufficient alone to initiate the self-heating process.

Two other important sources of heat must be considered:

- Moisture sorption when dry coal is put into contact with moist air.
- Pyrite oxidation in moist conditions.

Moisture is considered to play a important role on the oxidation rate of coal, especially by allowing catalytic effects when the pores are full of water.

2.2 Apparatus

A number of laboratory procedures have been used:

- Adiabatic Calorimeter

  This is designed to investigate the influence of moisture on the spontaneous heating of coal. The apparatus (Figure 1) is fully described by S. Pregermain in Publications Techniques No. 1, 1977, p. 39 - 43. It is noted that the Lee and Wardropper apparatus described in Section 3 is virtually identical.

- Reaction with Concentrated Hydrogen Peroxide

  This method, used as a quick procedure to detect the effect of pyrite, is fully described by S. Pregermain in Publications

Techniques, No. 2, 1972, p. 105 - 114. The apparatus used is shown in Figure #-2.

- Differential Thermal Analysis (D.T.A.) - Thermal Gravimetric Analysis (T.G.A.)

CERCHAR have an apparatus which combines D.T.A and T.G.A., used to compare coal reactivities in dry air (coal moist or dry).

The apparatus consists of two identical sample holders, one contains the sample, the other, an inert reference material (calcined alumina). The container are suspended from an accurate microbalance. An oven is raised around the sample and heated in a programmed manner. The differential temperature between the sample and reference is measured and any change in weight recorded.

2.3 Results

2.3.1 Adiabatic Calorimeter

- **Tests with Dry Coal and Dry Air**

The shapes of typical curves obtained by the apparatus when plotted on an Arrhenius diagram are shown in Figure E-3.

These show an initial decrease of the heating rate as a function of the temperature, due to the consumption of the more reactive sites. Then the heating rate increases in accordance with Arrhenius' Law. (Linear relationship between the log of the heating rate and the reciprocal of the absolute temperature).

The heating rate at a given temperature is mostly determined by the rank of the coal with low-rank coal being the most reactive. Fresh coal samples must be used.

- **Tests with Dry Coal and Moist Air or Moist Nitrogen**

Figure E-4 shows the shape of temperature-time curves under varying conditions.

There is an intitial fast increase of tempeature depending on the humidity of air or nitrogen followed by a plateau. In the cases where air is used, the temperature then starts to increase again at a rate following the Arrhenius Law (see Figure E-5). It should be noted from Figure A5-5 that the time to increase in temperature from 40°C to 100°C is much shorter than with moist air (4 hours 33 minutes) that with dry air (42 hours 30 minutes).

- **Tests with Moist Coal and Moist Air**

Figure E-6 shows how the quantity of pyrite affects heating rates. Humidity is thought to promote the oxidation of pyrite, especially the fine grained pyrite that can occur in some french coal seams. A case was mentioned of a mine where heatings occurred only when a high sulphur rider seam came into contact with the main seam. The oxidation of the pyrite initiated the self-heating process in the rest of the seam.

The reaction is described as:

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O = 2\ FeSO_4 + 2\ H_2SO_4 + 671\ Kcals.$$

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Iron sulphate produced catalyses the oxidation of coal.

These results on the adiabatic calorimeter are said to agreed with previous results obtained by the german reserchers, Beier, who observed in some cases much higher oxidation rates are obtained for high relative humidiites than for dry conditions (see Figure E-7).

2.3.2 Reaction With Concentrated Hydrogen Peroxide

The reaction is described as:

$$2\ H_2O_2 = 2\ H_2O + O_2 + 46\ Kcal.$$

The increase in temperature is mostly due to the decomposition of H_2O_2, catalyzed by pyrite and other salts.

From observed temperature/time curves (Figure E-8) an index I is determined by considering the time t_1 in minutes necessary to reach 90°C.

$$I = \frac{100}{t_1}$$

No relationship could be found between I and pyrite sulphur content (Spyr) but samples with Spyr greater than 2% have an I greater than 10. Coals with Spyr less than 2% are not considered susceptible from a sulphur content point of view. Figure E-9 shows the variation in Index I for different Spyr.

This reaction offers a quick method to detect pyrite at relatively high concentrations.

2.3.3 Combined T.G.A./D.T.A.

The effect of evaporation of moisture is thought to play a significant role in the development of heatings. When water vapour pressure in the air is less than that at the coal surface, evaporation of moisture take place producing a cooling effect.

D.T.A. experiments in an oxidizing atmosphere show an endothermic trough around 100°C representing the loss of water and it is suggested the longer the evaporation is delayed, the less is the chance of the development of a heating.

The tendency to self-heating can be characterized by a critical temperature T_C for which the value of the derivative $\frac{D(\Delta T)}{dt}$ is 0 (see Figure E-10). The higher the critical temperature, the less liable the coal is to spontaneous combustion.

No conclusions have been reached on the shape of the gravimetric curve.

It is thought that results from the T.G.A./D.T.A. are very dependent on experimental procedure, particularly the sample particle size and the packing density which affects moisture release through the sample. CERCHAR are considering an apparatus where individual particles of coal are completely separated to avoid this drawback. The test is not yet sufficiently proven to be used for comparison purposes and it is difficult to obtain reliable quantitve data.

The test is difficult to interpret as moisture desorption and oxygen absorption rates counter each other.

Results are not consistent - the same coal at different ash contents can give very different results. High ash coals can appear to be more reactive having a lower critical temperature.

2.3.4 Conclusions

CERCAR conclude that in a moist atmosphere, the coal is faced with any of the following three phenomena:

- oxidation
- oxidation and sorption of water vapour by the coal
- oxidation and desorption of water vapour from the coal

The thermal effects related to the absorption of moisture by the coal have an important bearing on its spontaneous heating.

Even when coal is in humidity equalibrium with air, the oxidation rate depends on the relative humidity of the system.

CERCHAR prefer to use the adiabatic apparatus for research purposes and to separate the effects of moisture and oxidation wherever possible. They have not considered use of multi-sample apparatus, but see merit in that conditions are standardized for several samples and time is saved.

2.4 Other Research

CERCHAR are also carrying out research into the storage of pulverized coal as described in Section 3 of the main report.

They are also developing a model for the behaviour of surface stockpiles but have not yet data for all the variables considered in the

model. They use a 1 m^3 test cell to obtain the low temperature limit for self-heating in storage.

3. PRINS MAURITS LABORATORY

3.1 Background

The visit took place on March 4, 1987.

Detailed discussions were held with Dr. A.H. Heemskerk and visits made to laboratory facilities.

The Prins Maurits Laboratory is part of a private organization for applied research known as TNO. It does research work mainly for government, but also for industry. It is divided into nine divisions for such disciplines as industrial technology, food, toxicology and defence. Defence is split into three, namely Physical (Electronics, etc.), Chemical and Industrial Human Engineering. The Chemical arm operates as the Prins Maurits Laboratory (PML). PML itself has nine working groups including explosion safety, gas/dust explosions, solid/liquid reactions, effect of explosions on surroundings, stability of materials, explosive effect of materials, explosive effects of reaction, etc. Dr. Heemskerk heads the solid/liquid working group, liasing closely with the Industrial Technology Department. Thus, there is a wealth of highly qualified and experienced scientific talent that can be applied to a particular problem of chemical reactions and kinetics.

The Dutch Government made a committment to coal as a third fuel in 1974 and has since built 3 large coal fired generating plants.

They decided to build substantial strategic coal stocks. Other industrial users also converted the coal and wanted information on coal storage.

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The government accordingly initiated a major research program to determine:

- Which coals would self-heat and why?
- What were the effects of self-heating and how could it be stopped?
- What was the loss of calorific value during storage and hence which was best coal to store on a long-term basis?

Other industrial companies that stored coal in the Netherlands also contributed to the study.

2.2 Work Program

Three working groups are assigned to study the self-heating problem.

PML carried out laboratory test swork.

The Ventilation group are developing a mathematical model of the reactions and air flow rates with a stockpile.

Power stations are cooperating by providing long-term test heaps of 10 tonnes each to validate the model.

2.3 Observations on Self-Heating

Dr. Heemskerk considered all coals subject to self-heating but moisture complicates the process. In a stockpile, moisture is critical as is ventilation.

If there is low ventilation by diffusion only, there is insufficient oxygen.

With high ventilation, the air provides sufficient cooling effect.

Intermediate air flow rates allow self-heating. He considers that mositure must be removed before self-heating turns to spontaneous combustion.

Heat generation processes consist of:

- Natural decomposition
- Formation of peroxides then alkydes, etc.
- Oxidation with internal oxygen particularly at higher temperatures (i.e. combustion can be sustained in some cases without outside oxygen)
- Oxidation with external oxygen

Moisture behaviour affects heat balance through:

- Evaporation
- Condensation
- Chemical processes (e.g. adsorption)

The PML have measured heat generation during chemical decomposition finding a relationship to rank. Steam coals produce 500 - 1200 mW/kg and lignites up to 5000 mW/kg.

4. LABORATORY METHODS

The methods used by Dr. Heemskerk are fully described in Report PML 1984-C35 attached.

The apparatus is also used for testing reaction heating of a wide variety of materials on behalf of the defence department and other industrial users. The test procedures are said to give extremely accurate results that are reproducible.

The isothermal storage test is most commonly used taking 4 - 5 days per test depending on the material. This time frame can be shortened substantially since only the first 4 hour after equilibrium is reached at 85°C is used in the comparison of coals.

The PML have built a number of multi-sample IST apparatus and have 8 sample and 6 sample equipment in use. A PC XT control and monitoring system is being installed that can handle up to 32 samples at once.

Attempts were made to convert the static IST method to a method with a gas flow through the coal. Results were obtained, but it was considered the loss of accuracy and reproducibility negated any perceived advantages.

The adiabatic apparatus with metal core is said to be extremely accurate and provide reproducible results. A test in the AST can take 3 - 4 weeks.

In discussion, Dr. Heemskerk stressed that accuracy takes time.

He does not believe in mixing the effects of moisture and oxidation. He believes since the effect of moisture is that of evaporation or condensation, the consequences can be calculated. Eventually, a coal will heat according to a certain rate once the moisture is removed at about 80 - 85°C. The problem, to some extent, with self-heating of coal is to prevent the coal from being dried and so allowing self-heating to proceed. For this reason, he generaly works on dried coal samples.

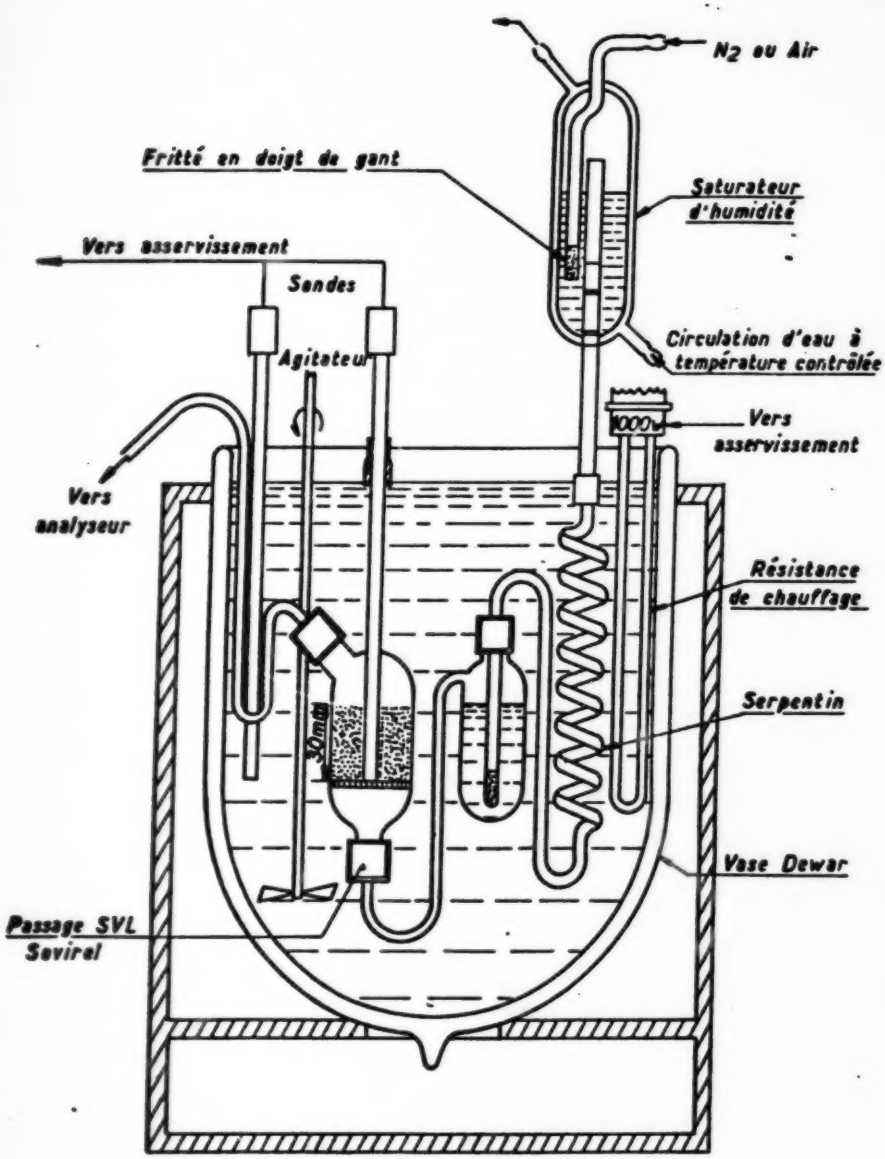
Because he does not like to mix the effects of moisture and oxidation, he also does not like any test that includes ramping of the temperature to force the reaction. He considers that theoretically and practically results are very hard to interpret even for an empirical type test.

5. CONCLUSIONS

The PML are an extremely accomplished group of scientists who have applied established experimental techniques to coal and obtained reproducible results on heats of reaction which are considered very accurate.

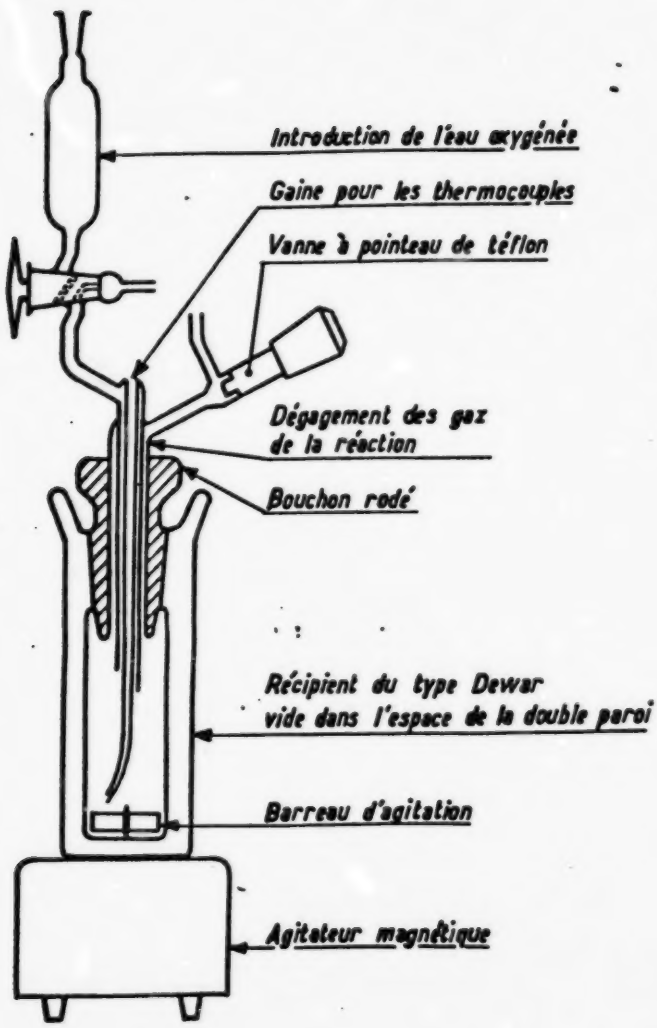
The IST is a static test that is readily adaptable to a multi-sample apparatus. If this were to be considered by CANMET, then it may be sensible to purchase basic equipment drawings from PML for manufacture in Canada. The IST would be difficult to adapt to flowing conditions. The adiabatic apparatus appears more accurate than other designs studied, but cannot be adapted to multi-sample.

FIGURE E-1
ADIABATIC TEST APPARATUS



Source: S. Pregermain, 1977

FIGURE E-2
APPARATUS FOR HYDROGEN PEROXIDE REACTION


Introduction de l'eau oxygénée
Gaine pour les thermocouples
Vanne à pointeau de téflon
Dégagement des gaz de la réaction
Bouchon rodé
Récipient du type Dewar vide dans l'espace de la double paroi
Barreau d'agitation
Agitateur magnétique

Source: S. Pregermain, 1976

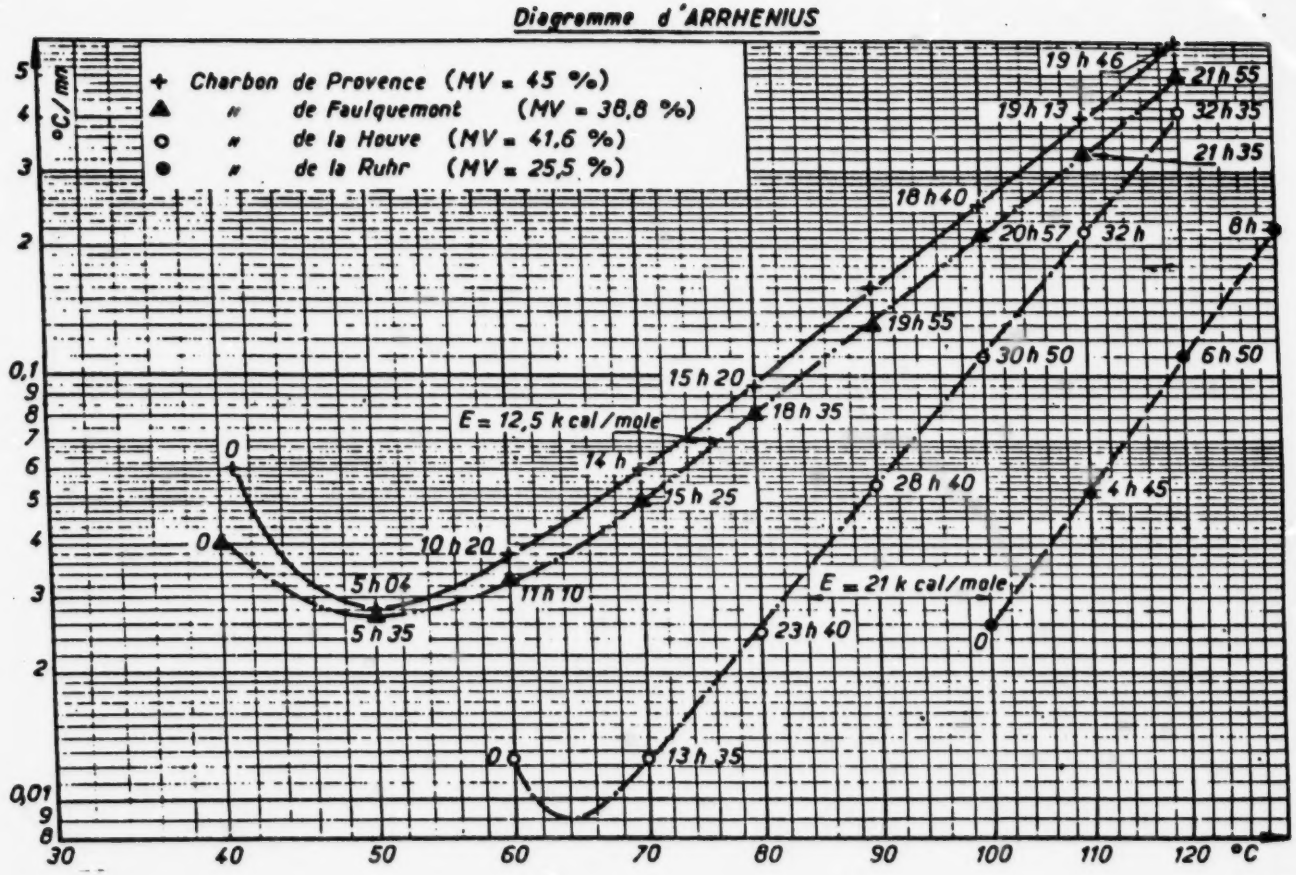
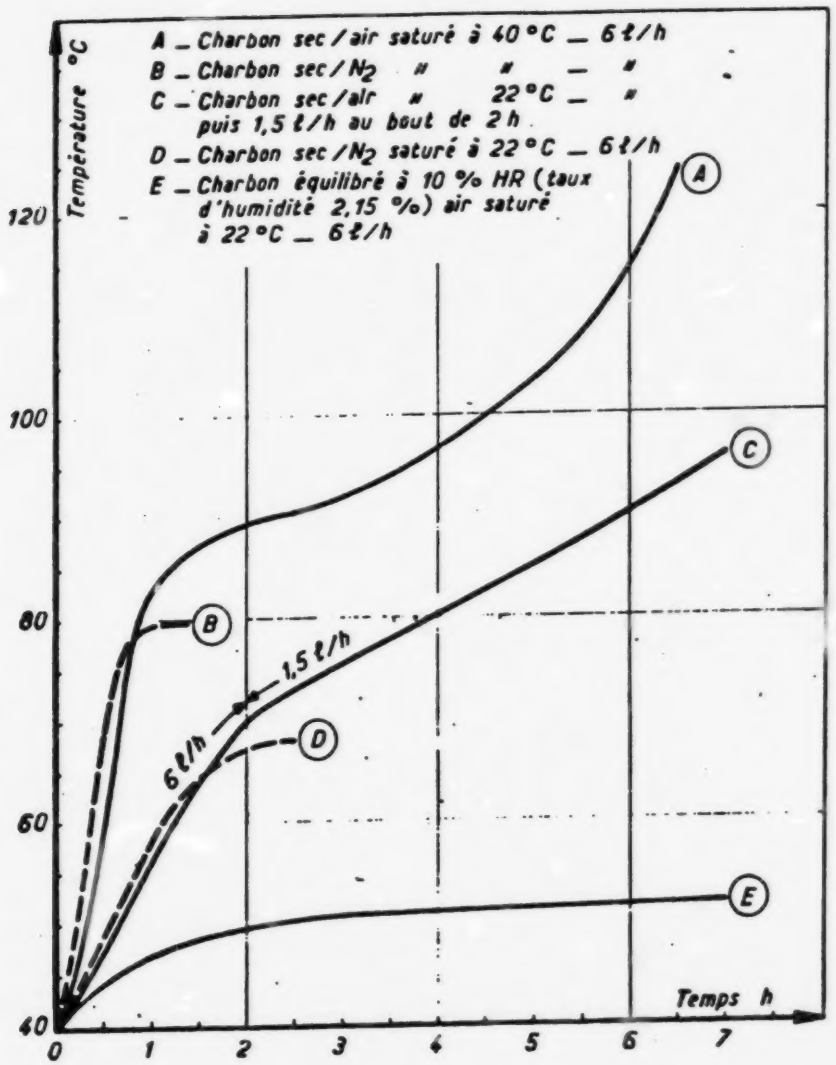


FIGURE E-3

ADIABATIC CALORIMETER - DRY AIR ON DRY COAL

FIGURE E-4

TEMPERATURE TIME CURVES AT VARIOUS MOISTURE CONTENTS



Source: S. Pregermain

FIGURE E-5
ARRHENIUS DIAGRAM

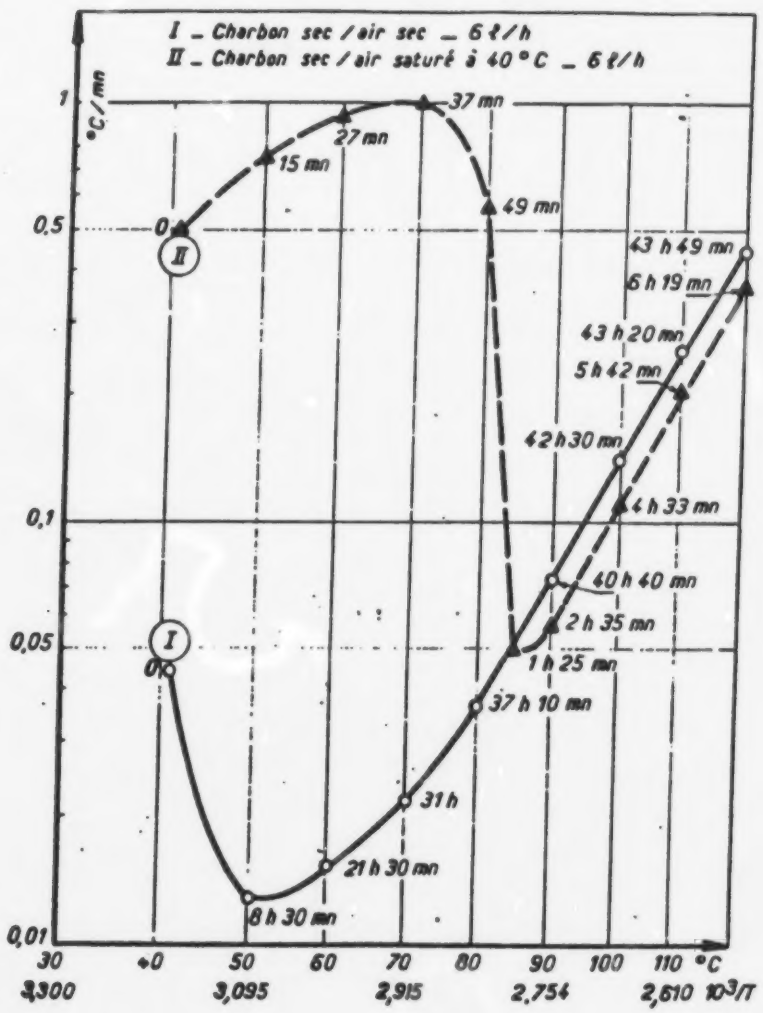
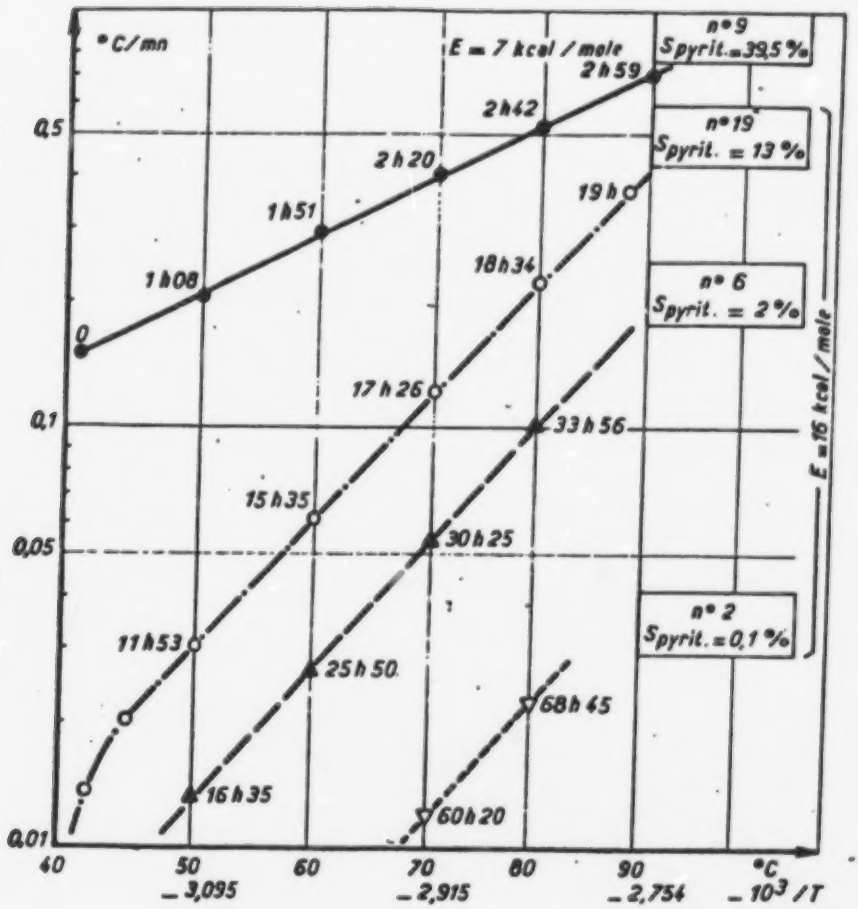
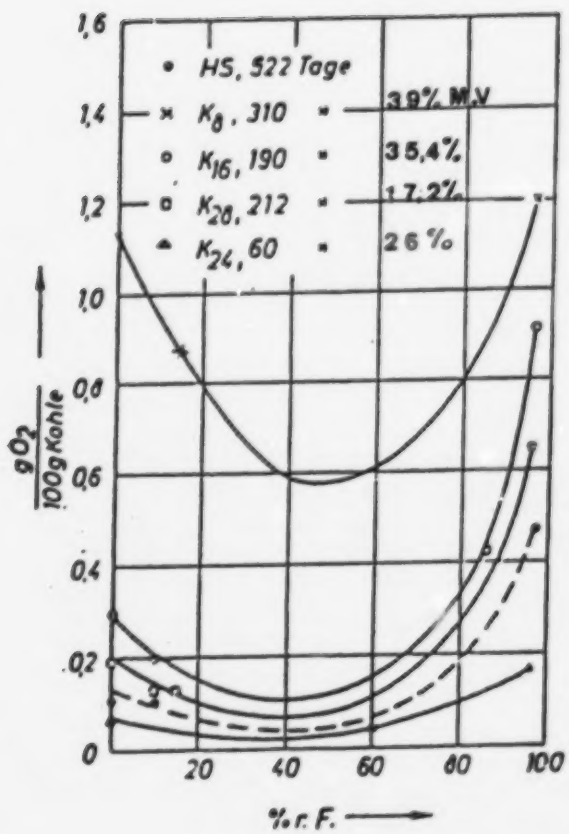


FIGURE E-6
EFFECT OF PYRITE ON HEATING RATES



Source: CERCHAR

FIGURE E-7
OXIDATION ABSORPTION AT VARIOUS RELATIVE HUMIDITIES



Source: E. Beier 4/1970, 81-88

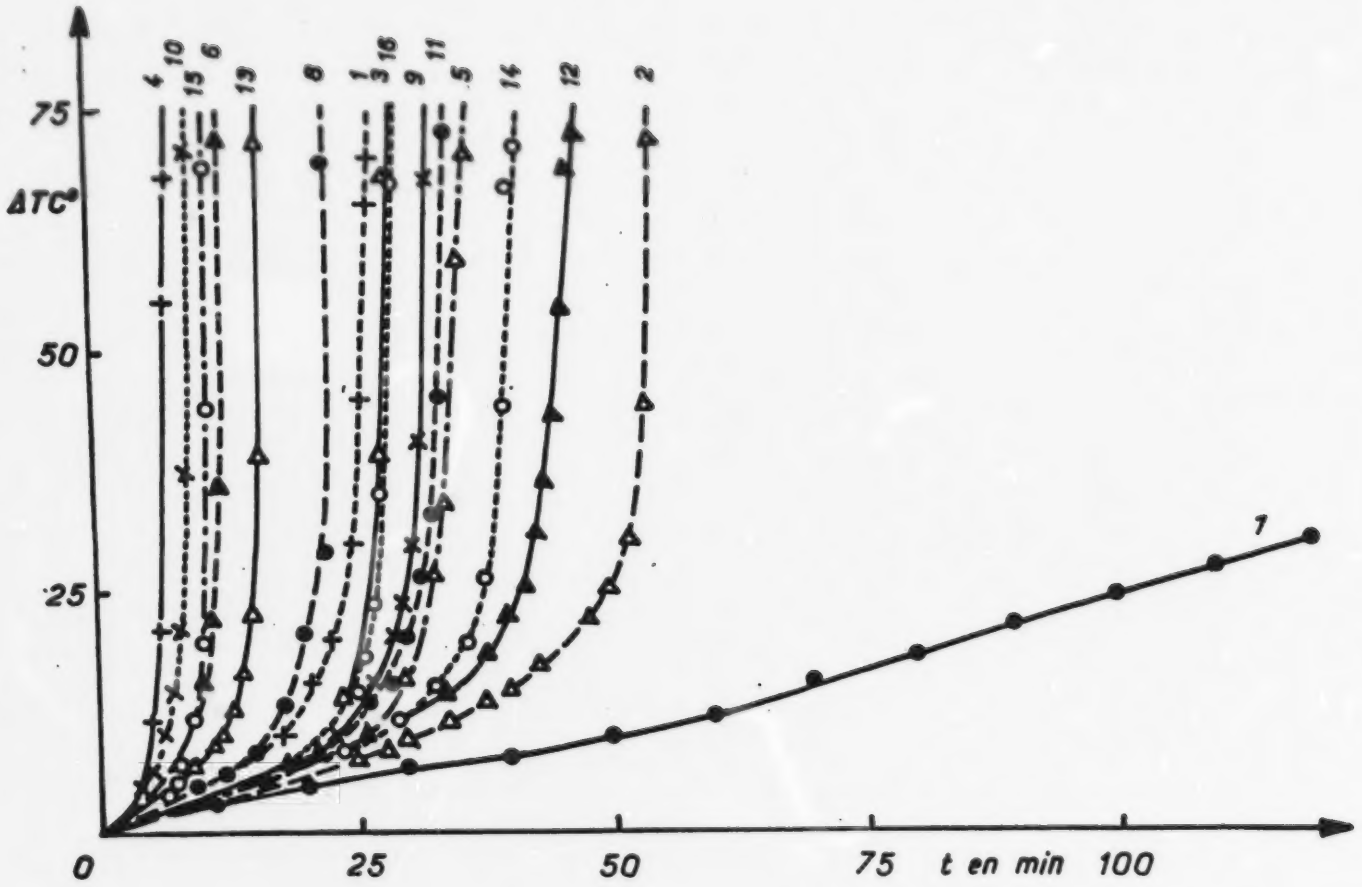


FIGURE E-8

REACTION WITH HYDROGEN PEROXIDE

Source: CERCHAR

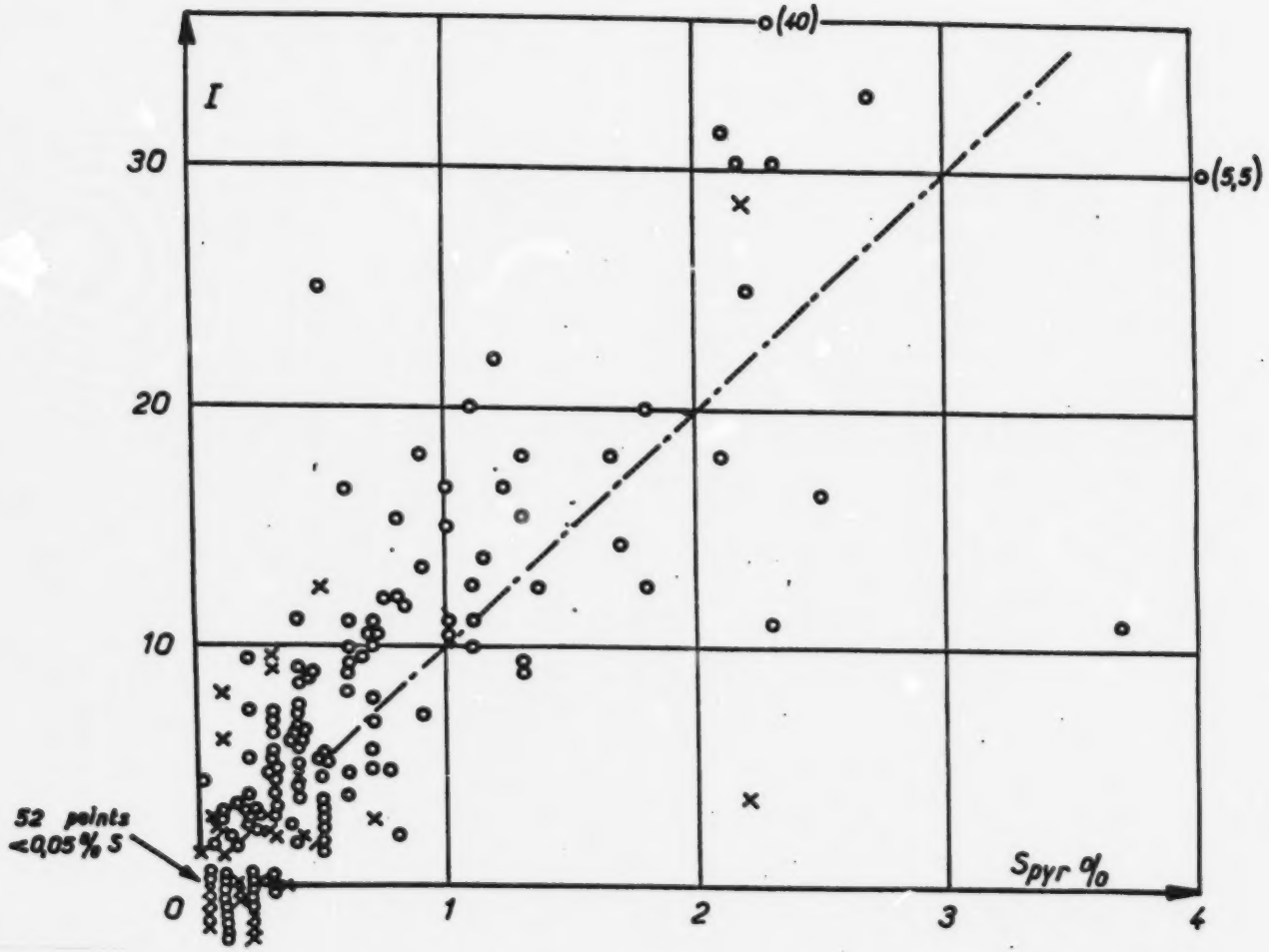


FIGURE E-9

VARIATION IN INDEX I GAS A FUNCTION OF PYRITE SULPHUR

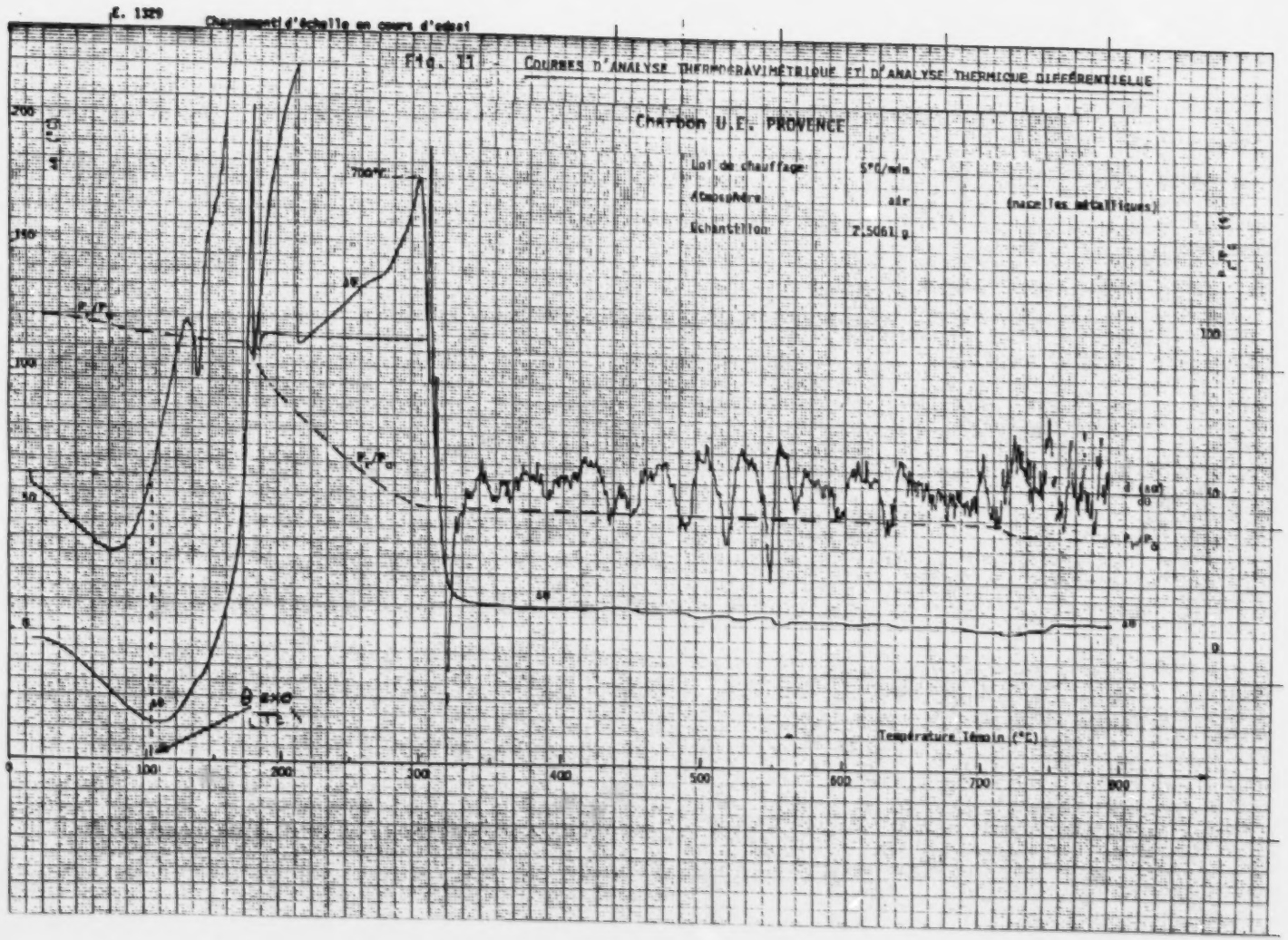


FIGURE E-10
DTA/TGA CURVE

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of copies:

SELF-HEATING OF SUB-BITUMINOUS COAL

- investigations 1983 -

A.H. Heemskerk

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This study has been performed under contract with the Bureau of Energy Research Projects, BEOP, in the frame-work of the Dutch National Research Program on Coal Technology, N.O.K.

Het onderzoek is uitgevoerd in opdracht van het Bureau Energie Onderzoek Projecten, BEOP, van de stichting Energie-onderzoek-centrum Nederland, in het kader van het Nationaal Onderzoekprogramma Kolen, N.O.K.

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ABSTRACT

The results of the investigation into the heat generation of coal which has been performed under contract with BEOP, are collected in this report. The relationship between the heat generation and the partial pressure of oxygen has been investigated for low oxygen concentrations (0-20% O_2). An unequivocal relationship could be established, which is in agreement with the observations at high oxygen concentrations (10-100% O_2).
The loss in caloric values and in the activity of the coal has been established with long-term storage experiments performed at 305 and 323 K. It appears that the addition of such chemicals as sulphuric acid and iron salts that are frequently encountered in coal piles stimulate the heat generation.
Adiabatic investigation reveal an equilibrium between the moisture in the gas phase and in the solid phase, leading to an adiabatic saturation temperature. This temperature is dependent on the flow rate and appears to remain between 348 and 363 K under normal storage conditions.
It is evident from all experiments that the entire process of self-heating is determined by the chemical oxidation process generating heat and the physical process of evaporation consuming heat.

SAMENVATTING

In dit rapport zijn de resultaten gebundeld van het in opdracht van BEOP uitgevoerde onderzoek naar de warmteproduktie van steenkool.
Onderzocht is de invloed van de zuurstofconcentratie op de warmteproduktie in de kool bij lage zuurstofconcentraties (0-20% O_2). Een eenduidige relatie kon worden vastgesteld die aansluit bij de waarnemingen bij hoge zuurstofconcentraties (20-100% O_2).
Het verlies in stookwaarde en de teruggang in activiteit van de kool is vastgesteld via proeven aan een langdurige opslag van de kool bij 305 en 323 K. Tevens is vastgesteld dat de aanwezigheid van enkele regelmatig bij koolopslag voorkomende stoffen als zwavelzuur en ijzer, de warmteproduktie beïnvloedt.
Uit adiabatisch onderzoek blijkt dat het doorleiden van lucht leidt tot een evenwicht tussen het vocht in de gas- en vaste fase bij een adiabatische verzadigingstemperatuur. Deze temperatuur, die afhankelijk is van het debiet van de gasstroom blijkt bij normale opslagcondities ongeveer 348-363 K te zijn.
Uit de metingen blijkt duidelijk dat het broeiproces geheel wordt bepaald door een warmteproducerend proces (de exotherme oxidatie van kool) en een

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ANNEX I

ANNEX II

ANNEX III

1. GENERAL INTRODUCTION

Investigations performed in the Prins Maurits Laboratory TNO in the period 1981-1983 (1,4), showed that the self-heating of coal is a result of two major processes: a chemical process in which the coal is oxidized and a physical one in which water is either evaporated from or condensed on (absorbed to) the coal. Both processes can either oppose or amplify one another.

The major processes are affected by several parameters amongst which the temperature, ventilation rate, particle size, chemical composition, etc. Most of these parameters are interrelated. For example, as the local temperature increases free convection is stimulated through the coal which leads to higher ventilation flow rates. The increased ventilation rate supplies an additional amount of oxygen to the coal and enables in this way a sustained increase in the reaction rate.

Small particles with large surface areas (coal dust) can be whirled up in ventilation draughts. The combination of elevated temperatures and ignition sources can bring about sustained self-heating, open fire or even dust explosions. The susceptibility of coal to the process of self-heating has been investigated by determining the self-heating properties under isothermal and adiabatic conditions in a study performed under contract with the Bureau of Energy Research projects (BEOP).

These investigations have been carried out with several types of coal in the Isothermal Storage Test (IST) and in the Adiabatic Storage Test (AST). The investigated coal types were sub-bituminous coals of American and Australian origin. A part of the study has already been described in reports PML 1982-112 (1) and PML 1983-107 (4).

In chapter 3 of the present report the investigations into the relation between the partial pressure of oxygen and the heat generation on the behaviour of water throughout the self-heating process, on the caloric losses and the decay in coal activity during long-term storage, and on the effects of chemical additions to and ventilation through the coal are being discussed.

The conclusions resulting from the investigations are discussed in chapter 4 and the recommendations are summed up in chapter 5.

Coal characteristics are given in several annexes.

2. EXPERIMENTAL EQUIPMENT

2.1 Isothermal Storage Test (IST)

In the Isothermal Storage Test (IST) the heat generated at constant temperature by reacting of decomposing substances is measured as a function of time. Performance of these measurements at a series of temperatures leads to a quantative understanding of the relation between the temperature and the heat generation of the substance under investigation. The IST is applicable to solids, liquids, pastes and dispersions.

The IST shown in Fig. 2.1 consists of a large heat sink (an aluminum block) which is kept at a constant temperature. In the block are two holes with a heat flow meter (e.g. a Peltier element) at the bottom of each hole. Holders are placed on both heat flow meters. These holders are identical. One holder contains the sample, the other an inert substance.

The heat generated by the sample results in a voltage signal from the heat flow meter which is proportional to the heat flow. Random fluctuations in the heat flow are avoided by monitoring the voltage difference between both heat flow meters.

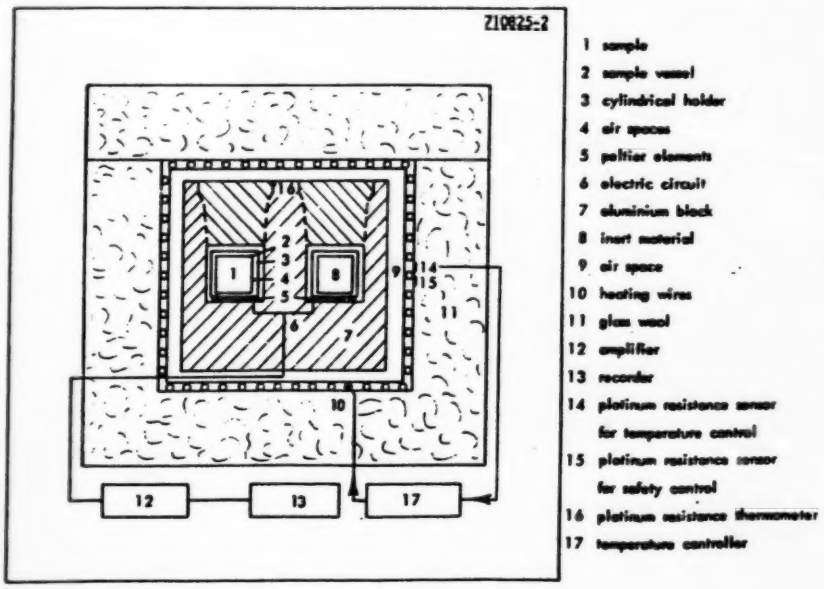

Fig. 2.1 Cross-section of the Isothermal Storage Test (Arch.no. 710825)

The stainless steel sample holder has a volume of 70 cm^3. The sample mass amounts to about 20 g. Measurements can be performed in the temperature range from 250 K to 420 K. Heat generations can be measured between the lower limit of 5 mW/kg and the upper limit of 5 W/kg with an accuracy of at least 30% in the lower range to 5% in the higher ranges.

2.2 Adiabatic Storage Test (AST)

In the Adiabatic Storage Test (AST) the heat generated at nearly adiabatic conditions by reacting or decomposing substances is determined as a function of time. The AST is applicable to solids, liquids, pastes and dispersions.

The AST shown in Fig. 2.2 consists of a $1{,}5 \times 10^{-3}$ m^3 Dewar vessel sealed with a stainless steel lid. This lid is provided with insulating material on the inside. The Dewar vessel is placed in an oven. The temperature of the oven is kept equal to the temperature of the sample in the Dewar vessel. In this way the heat loss is kept at a minimum and a nearly adiabatic condition is created

An internal electric heating coil is used to heat the sample to the desired initial temperature. The heating coil is also used to determine the specific heat of the sample.

A gas can be led through the Dewar vessel by means of tubes passing through the lid of the vessel. From the inlet tube the gas is spread over the bottom of the Dewar vessel. The gas outlet is at the top of the Dewar vessel. Thus the entire sample is brought into contact with the gas. Before being supplied to the Dewar vessel the gas is carefully thermostated at a temperature equal to that of the sample. Because of the nearly adiabatic conditions (the maximum heat loss is 10 mW) the heat generated by the sample is almost completely converted into an increase in temperature of the sample. Therefore, the temperature of the sample is recorded continuously as a function of time. From the increase in temperature in relation to the specific heat and the mass of the sample the heat generated by the sample can be determined.

An experiment is discontinued when the heating rate is too fast. In this case the system is cooled down with the aid of a cooling coil. Measurements can be performed in the temperature range from 250 K to 470 K.

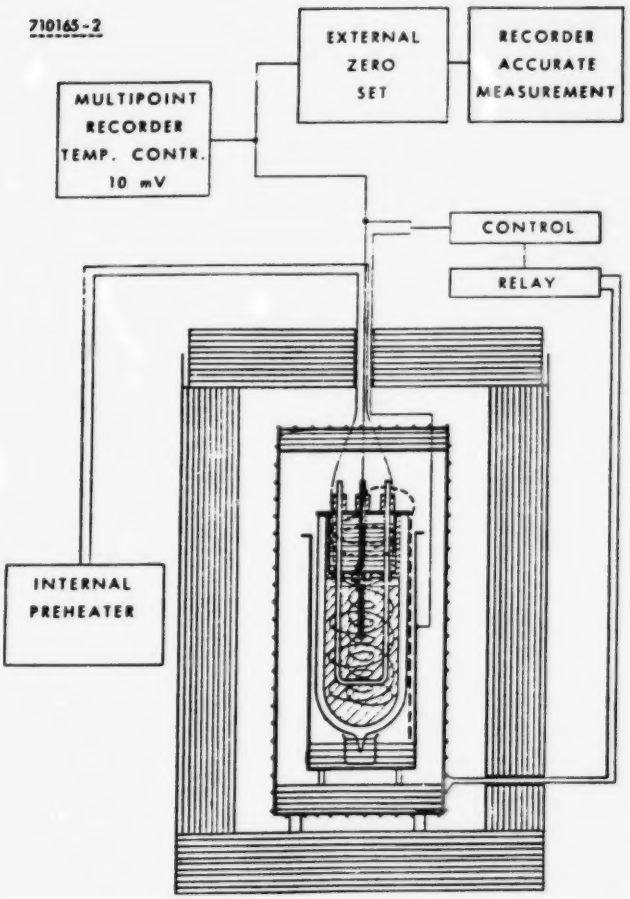

Fig. 2.2 Arrangement of the Adiabatic Storage Test (AST)
(Arch.no. 710165)

Even at relatively low temperatures small heat generations can be determined. The smallest temperature increase that can be determined corresponds to a heat generation of 15 mW/kg. The upper limit is determined by the capacity of the cooling coil. If water is applied as coolant a maximum heat generation of 500 W is allowed. The accuracy of the measurements is at least 30% at 15 mW/kg and 10% from 100 mW/kg to 10 W/kg.

3. EXPERIMENTAL RESULTS

3.1 Introduction

The investigations into the self-heating of sub-bituminous coal performed in 1983 were carried out with three types of coal. Two of the coal samples were of Australian origin. This coal is stored semi-permanently at the "Amercentrale". The storage period will at least last a few years. In the report these two samples are referred to by the serial numbers K3 and K4. The proximate analysis of both samples is shown in the annexes I and II, respectively. Both coals have almost equal caloric values. The water content of sample K3 is rather high. The third coal sample, which is of American origin, is referred to by the serial number K5. The proximate analysis of this coal sample is shown in annex III.

All coal has been supplied by the KEMA and imported by coal-fired power-stations.

The particle size of the coal investigated in the IST varied between 1,2 and 2,0 mm diameter. The influence of the particle size was investigated in 1981 (1) and 1982 (4,6). The moisture in coal piles is often acidic and mostly contains sulphuric acid. The influence of an acidic environment on the heat generation has been investigated in the IST.

The influence that ventilation draughts exert on the heat accumulation within a coal pile has been simulated by adiabatic experiments. The ventilation flow rates varied between 0,5 and 4,0 l/hr which corresponds to linear velocities between $2{,}0.10^{-5}$ and $1{,}6.10^{-4}$ m/s.

The influence of the oxygen depletion on the experimental results obtained in the AST has been investigated and appeared to occur only at low air velocities and high reaction rates (corresponding to temperatures in the coal of well above 373 K).

3.2 Isothermal storage experiments

3.2.1 Influence of oxygen on the heat generation

The relation between the concentration of oxygen in the gas surrounding the coal particles and the heat generated by the coal as a result of the degradation process has been investigated with two types of coal, viz. the types K3 and K5. In addition to experiments in former years (1,4) this relationship has now been established for the concentrations of oxygen below 20%.

From the experiments performed in 1981 and 1982 (1,4) it appeared that the oxygen absorbed to the coal has a large influence on the heat generation, especially at low oxygen concentrations. To avoid complications due to the oxygen adsorption all coal in the investigations were carefully prepared under nitrogen.

To create a large virgin surface area large lumps of coal of type K3 were ground under nitrogen into coal dust. From the coal dust the fraction with particle sizes between 1,2 and 2,0 mm were separated by sieving the coal under nitrogen. This fraction was kept in a nitrogen flow up to the moment the isothermal experiments started. The period under nitrogen flow was at least two days.

The actual isothermal experiments started by weighing the exact amount of prepared coal (again under nitrogen) and contacting the coal sample with a gas mixture of nitrogen and oxygen containing the desired oxygen concentration. After that the coal sample was treated in the isothermal storage test. Consequently, pretreatment and storage of the coal took place under nitrogen and a large surface area was created free from absorbed oxygen. The heat generated at 338 K and at 358 K by coal of type K3 which had been handled in the above-described way, is shown in Fig. 3.1 and 3.2, respectively.

It appears that the greatly enlarged virgin surface area of the coal has resulted in an increased activity of the coal for all oxygen concentrations. This increased activity clearly appears from Table 3.1 in which the heat generations of both crushed and non-crushed coal (1) are shown.

Table 3.1 Heat generated under nitrogen by crushed coal (K3*) and by non-crushed coal (K3)

Oxygen concentration (%)	Heat generation of		
	sample K3* at 338 K (mW/kg)	sample K3* at 358 K (mW/kg)	sample K3 at 358 K (mW/kg)
0	41	33	105
5	203	211	-
10	323	501	80
20	413	991	200
100	469	2253	500

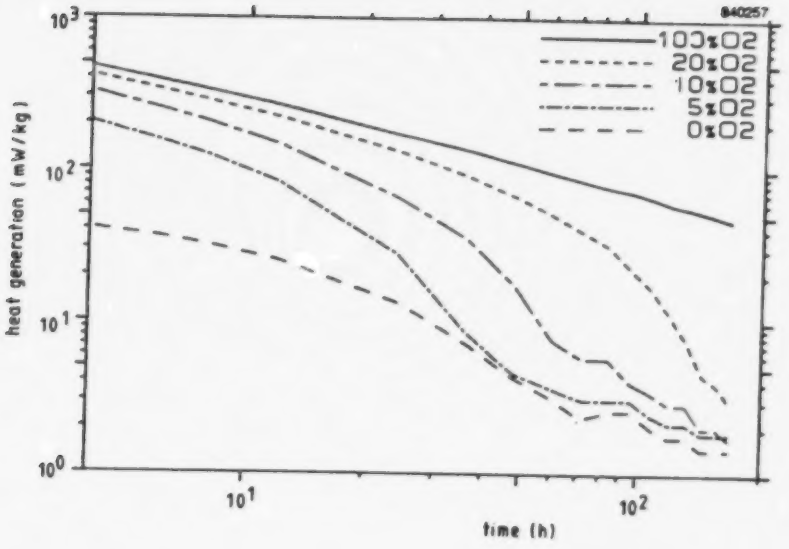

Fig 3.1 Heat generation of coal type K3 at 338 K as a function of oxygen concentration and time (Arch.no.840257)

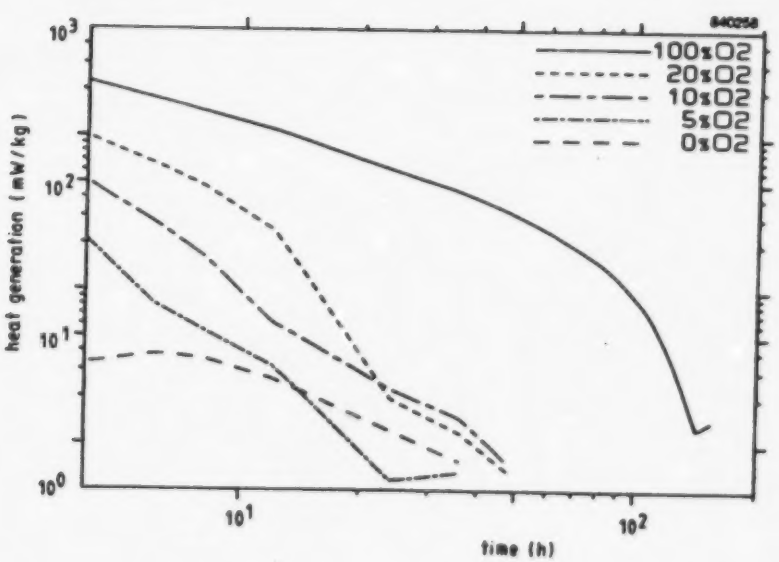

Fig. 3.2 Heat generation of coal type K2 at 358 K

In the experiments with non-crushed coal (K3) no precautions were taken with regard to oxygen adsorption to the coal. Coal dust with particle size between 1,2 and 2,0 mm was sieved, weighed to the correct amount and immediately contacted with the desired concentration of oxygen. Therefore, the coal in these experiments had an ample amount of oxygen adsorbed to it, which in the case of low environmental concentrations of oxygen resulted in a relatively high activity of the coal. In the case of high environmental concentrations of oxygen the relative shortage of active sites resulted in a limited heat generation. Both aspects influence the relation between oxygen concentration and heat generation.

The coal which had been crushed before use ($K3^*$) shows a stronger influence of the oxygen concentration on the heat generation. A sufficiently high oxygen concentration even leads to an increase in the heat generation by a factor 4 to 5 (cf. the heat generations for oxygen concentrations higher that 10% in Table 3.1). Even at a lower temperature (338 K) the activity of the $K3^*$ sample appears to be higher under the same conditions. Insufficient oxygen (concentrations up to 10%) leads to an oxygen-controlled activity whereby the temperature is only of minor importance (cf the heat generations for oxygen concentrations lower than 10% in Table 3.1). In these cases the oxygen adsorbed to the coal results in a considerably higher heat generation under similar conditions.

The relationship between the heat generation and oxygen concentration is shown in Fig. 3.3 and 3.4 for the coal degradation performed at 338 K and 358 K, respectively. The conditions in the IST are such that it may be assumed that the temperature in the coal is uniform, that the migration of oxygen is amply sufficient and that the active sites are uniformly spread throughout the coal. Furthermore, the heat of reaction, the reaction rate and the amount of active sites on the coal remain approximately constant at constant temperatures and for small degrees of conversion. Under these conditions the relation between the heat generation (q_w) and the partial pressure of oxygen (p_z) can be described (4) by

$$\ln q_w = n \cdot \ln (p_z) + \ln (k) \qquad (3.1)$$

where the power coefficient n and the multiplicator k are constant.

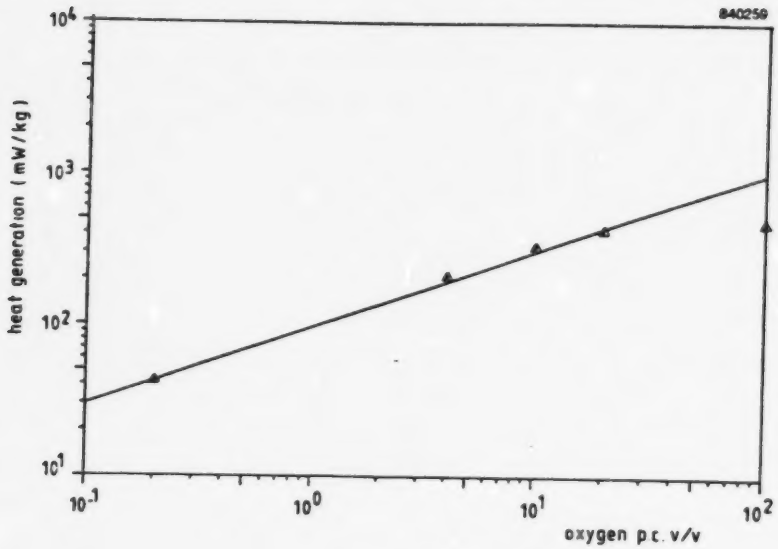

Fig. 3.3 Relationship between the heat generation and the oxygen concentration obtained with coal type K3 at 338 K (Arch.no. 840259)

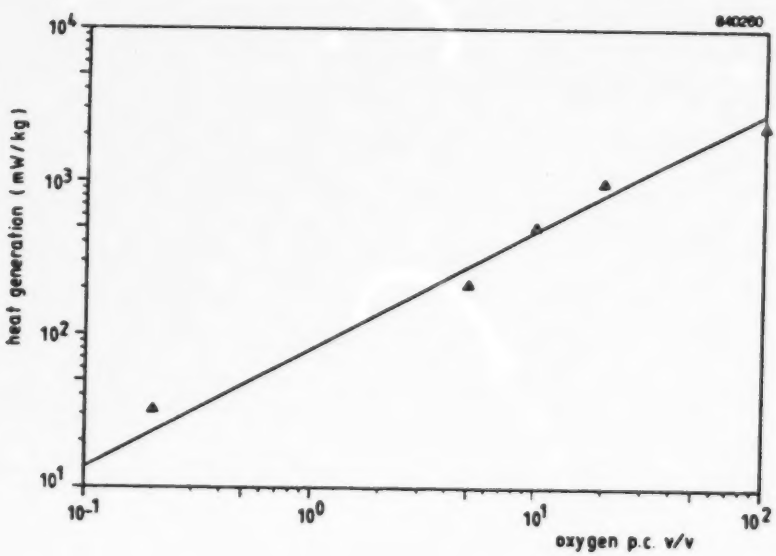

Fig. 3.4 Relationship between the heat generation and the oxygen

From the experiments with crushed coal (K3*) it appears that the value of the power coefficient n is dependent on the temperature. This value is 0,77 and 0,51 for temperatures of 358 K and 338 K, respectively. From previous experiments with high concentrations of oxygen the average value of n was found to be 0,7 at a temperature of 358 K and somewhat lower at 338 K (cf. (4), Fig. 3.8). Thus, the values of n obtained in experiments with relatively high and relatively low pressures of oxygen agree with one another. The anomaly in this value which was previously encountered can indeed be imputed to the adsorption of oxygen to the coal causing a relatively high initial activity of the coal and resulting in relatively high initial heat generations.
The relationship between the heat generation and the oxygen pressure has been determined with coal of type K5 as well. The preparation of the coal sample differed slightly from the preparation of the K3 samples. The K5 samples were not crushed, but only sieved to obtain a fraction with particle size between 1,2 and 2,0 mm. All handling of the K5 coal (including storage) took place under nitrogen. Moreover, the coal was exposed to a nitrogen flow for a period of two days before the actual IST experiments took place.

The relationship between heat generation and time obtained in the experiments with several concentrations of oxygen, is shown in Fig. 3.5. The ratio of the heat generated by the coal samples of K5 and K3 is 3 : 1, which is identical to the ratio encountered in previous experiments under similar conditions (4).
The relationship between the maximum heat generations and the oxygen concentrations resulting from the experiments is shown in Fig. 3.6. This relationship too, appears to be exponential. However, in this case the power coefficient appears to be 0,34. The heat generation at an oxygen concentration of 100% which is calculated using the exponential relationship (approximately 1,1 W/kg) is in agreement with experiments performed in 1982 (4).

On the basis of the experiments eq. (3.1) can be applied to the extrapolation of results and to the calculation of the influence of oxygen on the heat generation for all concentrations of oxygen. Therefore, the results of the experiments performed at high oxygen concentrations in the IST (up to 100%) can be extrapolated to the conditions encountered during storage.

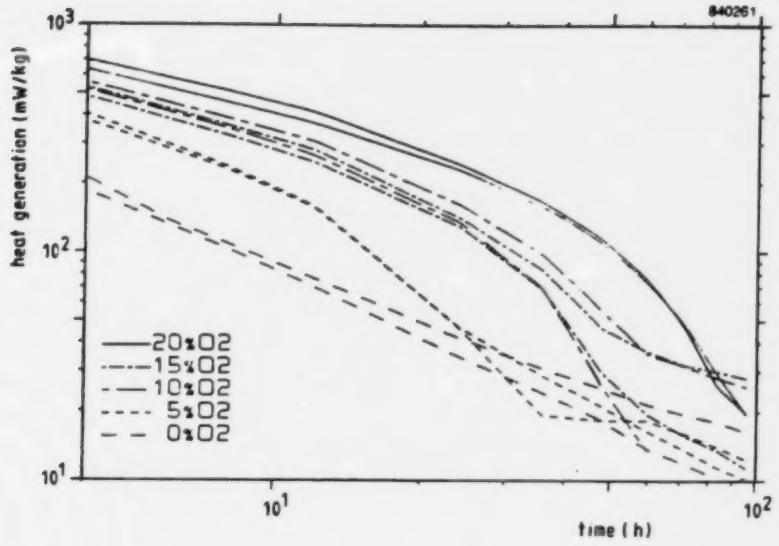

Fig. 3.5 Heat generation of coal type K5 at 358 K as a function of oxygen concentration and time (Arch.no. 840261)

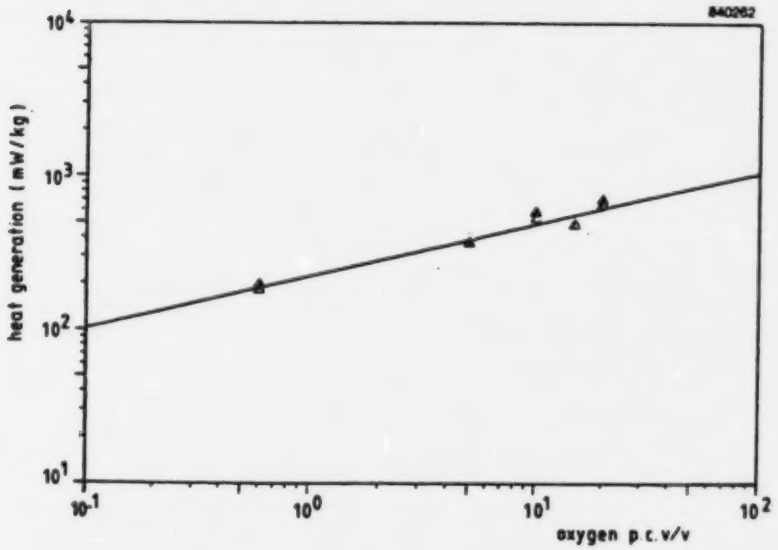

Fig. 3.6 Relationship between heat generation and oxygen concentration obtained with coal type K5 at 358 K

3.2.2 Caloric losses in sub-bituminous coal during long-term storage

In order to determi the caloric losses in sub-bituminous coal during long-term storage samples of about 4 kg of coal of the types K4 and K5 were stored at constant conditions. Storage started January 1983 and took place at two temperature, 305 K and 323 K. the store-rooms were ventilated by free convection. Care was taken to precondition the incoming air to the same temperature and humidity as the air in the store-rooms.

Despite these precautionary measures the stored coal gradually lost its water content. This was perceptible in both types, though most pronounced in type K4 whose water content decreased from 7,2 to less that 1% in a period of 9 months.

The decay in caloric value for both types of coal has been established by determining the heat of combustion of the original coal and that of the stored coal. The determination of the heat of combustion and the calculation of the caloric value of the coal occurred entirely in accordance with NEN-ISO 1928 (3) and was carried out in an adiabatic calorimeter at constant volume. For alle determinations 300 mg coal was weighed into a crucible and pressurized to the prescribed pressure of oxygen. The coal was ignited by a nickle-chromium ignition-wire and some gun-cotton. The calculated heat of combustion was corrected for the heat of combustion of these materials. The caloric value of the coal was calculated on the basis of the net weight of coal (i.e. without moisture) but including an average moisture content in the coal during normal combustion. The average moisture contents of coal types K4 and K5 were 7,2 and 3,2 %, respectively. The caloric values thus obtained are shown in Table 3.2

Table 3.2 Caloric values of sub-bituminous coal, types K4 and K5, before and during long-term storage

	Caloric value of	
	Coal type K4 (mJ/kg)	Coal type K5 (mJ/kg)
Original coal	26,6	29,8
After storage at 305 K	25,7	28,2
After storage at 323 K	23,7	26,4

The decay in the caloric value of the coal types K4 and K5 which were stored at 305 K, is 3,4 and 5,4 %, respectively. During storage at 323 K this decay amounts to 10,9 and 11,4 %, respectively. These values indicate that coal type K5 shows a higher activity at lower temperatures in contrast with coal type K4, which has a higher activity at higher temperatures. This is in agreement with the ratio of maximum heat generations (4).

A comparison between the decays at 305 K and 323 K is intricated. Although the caloric loss which is to be expected theoretically, can be described by

$$\Psi = \int_0^t Z.c.p^n.\exp\ \frac{-E}{RT}\ .\ dt \qquad (3.2)$$

and the ratio between the decays at 305 K and 323 K by

$$\frac{\phi_\infty - \phi_{305}}{\phi_\infty - \phi_{323}} = \frac{\Psi_{305}}{\Psi_{323}} \qquad (3.3)$$

it appears to be difficult to solve these equations. This is mainly caused by the unknown behaviour of the oxygen pressure and the concentration of coal which is active in the degradation process. Both parameters are functions of temperature, time and degradation itself and these functions can only be approximated very roughly. Based on the average activation energy of the "coal reaction" and on the temperatures applied during storage the amount of coal degraded at 323 K may be expected to exceed the amount of coal degraded at 305 K by a factor between four and five. In practice this factor is bound to be lower because the higher oxygen consumption and the faster decay of the coal at 323 K. Taking into account the average partial pressure of oxygen and the average extent of the coal reaction it appears that the factor may certainly be overestimated by 20%.

If the average temperature in a large-scale coal storage is assumed to be 300 K the maximum yearly loss in caloric value may be approximated at 5% for this kind of sub-bituminous coal in the first year of storage.

3.2.3 Decay in coal activity

The decay in the coal activity as a result of the long-term storage degradation has been determined with the coal types K4 and K5. The activity has been determined with IST-experiments at 358 K in vessels filled with air. The coal used in the experiments was drawn in small samples from the long-term storage samples of 4 kg. Subsamples (mass 5 g) with particle sizes between 1,2 and 2,0 mm were sieved from the samples for direct use in the IST. For each storage temperature the heat generation was measured with two portions of each subsample. The heat generated by the similar subsamples obtained in the way mentioned above varied because of the relatively poor representativity of each of the samples. However, the rather small amount of coal in storage did not permit a more representative way of sampling.

The heat generations obtained with the K4 samples are shown in Fig. 3.7, those obtained with the K5 samples in Fig. 3.8. The maximum heat generations averaged for each of the storage temperatures are shown in Table 3.3, together with the heat generated under equal conditions by both coal types before the long-term storage started.

A comparison of the heat generations of the coal types K4 and K5 shows that both types suffer similar decreases. However, aging of the coal cannot be extrapolated with sufficient accuracy from the two values measured up to now. Based on the values obtained so far it appears that the aging influences the heat generated by the coal. The results indicate that the losses in the first year will be maximum, the losses in the second year may be estimated to decrease by 20 to 30%.

Table 3.3 Heat generated in the IST by the coal types K4 and K5 after long-term storage

Storage temperature	Heat generation of	
	coal type K4 (mW/kg)	coal type K5 (mW/kg)
Originally	330	450
323 K	150	272
305 K	272	391

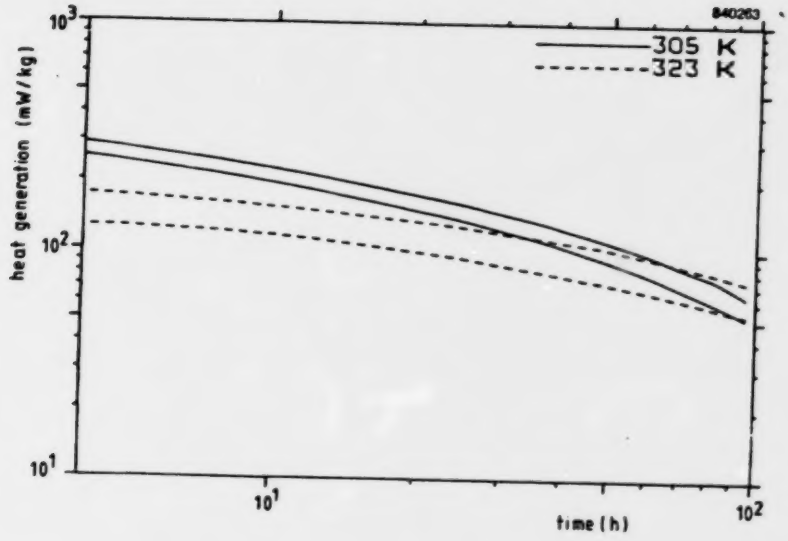

Fig. 3.7 Heat generations of coal type K4 after long-term storage at temperatures of 338 K and 358 K (Arch.no. 840263)

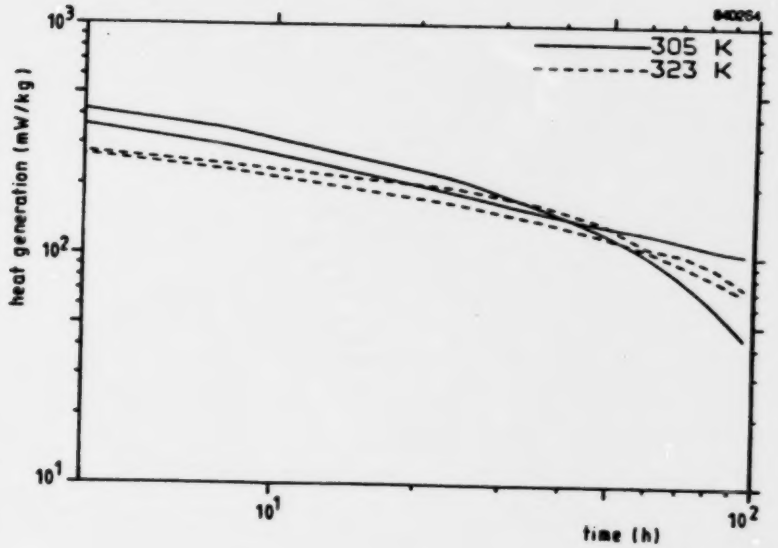

Fig. 3.8 Heat generations of coal type K5 after long-term storage at temperatures of 338 K and 358 K (Arch.no. 840264)

3.2.4 Influence of chemicals on the heat generation of coal

The influence of chemicals on the heat generation of coal has been investigated qualitatively in the IST. The dope chemicals investigated include sulphuric acid, iron (II) sulphate, iron (III)sulphate and ammonium hydroxide.

The incidence of acids during coal storage is often overlooked, but sulphuric acid is frequently encountered and its acid concentration can be high (pH < 1). The influence of these occurrences on the heat generation has been neglected until now.

The influence of oxidative or reductive environments on the heat generation of the coal, especially in combination with the frequently encountered iron ion is uncertain.

The influence of such environmental effects on the heat generated by the coal has been investigated qualitatively by measuring heat generations obtained with "doped" coal. In each case of 20 g of coal was doped by leaving the slightly wet coal in the desired chemical solution for a period of 24 hours. The coal was then filtered and dried for approximately three hours in an air flow of low humidity at a flow rate of 0,35 m^3/hr. The treated coal was partly used for IST experiments and partly to determine the amount of chemical absorbed to the coal. The solution used in the acid treatment was a 2M sulphuric acid solution resulting in a final amount of 16,5 g of acid per kg coal. In the case of Fe (II) the use of a saturated $FeSO_4$-solution (0,1 M) resulted in an amount of 29,8 g of $FeSO_4$ per kg coal and in the case of ammonia a saturated NH_4OH solution led to a final amount of 0,37 g of NH_3 per kg coal. In the case of Fe (III) a slightly modified preparative methode was used. In this case an amount of Fe (III) sulphate (the molar amount equal to that of Fe (II) in the case mentioned above) was ground together with slightly wetted coal. After a period of 24 hours the coal was dried in an air flow. The amount of $Fe_2(SO_4)_3$ appeared to be 20,43 g per kg coal.

The heat generations measured in the IST with various doped and virgin coal samples are shown in Table 3.4 and Fig. 3.9.

From Table 3.4 and Fig. 3.9 it is evident that the additions to the coal tend to increase the heat generation to a varying extent. However, the effect is puzzling. Both acid and base have an approximately equal effect on the heat generation and nearly triple the original value.

Table 3.4 Maximum heat generated by chemically treated coal measured in the IST during storage under air

Dope chemical	Heat generation (mW/kg)	Relative increase (%)
NH_4OH	810	2,5
H_2SO_4	805	2,4
$Fe_2(SO_4)_3$	450	1,4
$FeSO_4$	380	1,2
-	330	1,0

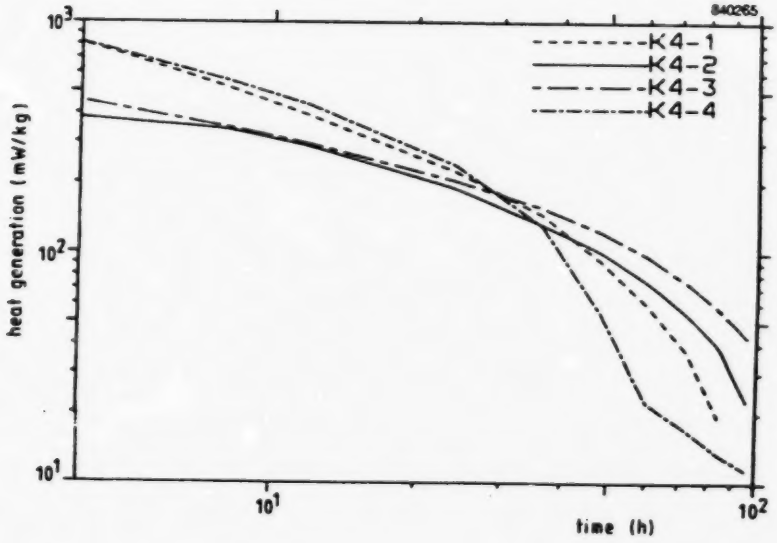

Fig. 3.9 Heat generation of sub-bituminous coal carrying various chemical additives

K4-1: additive sulphuric acid

K4-2: additive ammonium hydroxide

K4-3: additive iron (III) sulphate

K4-4: additive iron (II) suphate

(Arch.no. 840265)

The influence of iron in either the reductive or the oxidative state is approximately equal as well, but the effect remains relatively small. From these experiments it may be concluded that the formation of sulphuric acid in the coal piles as often encountered in a large-scale coal storage strongly stimulates the heat generation. This effect may lead to large local increases of the temperature.

3.2.5 Behaviour of moisture and its influence on the IST experiments

Up to now the relationship between the oxygen concentration and the heat generation of the coal has been established by measuring the initial, i.e. maximum heat generation. The amount of oxygen in the closed sample vessel remains more or less constant because of the short measuring period at these conditions and no substantial changes in the pressure other than temperature-dependent ones occur.
However, in the course of a complete IST experiment the heat generation will decrease as a result of the decreasing pressure of oxygen (1). It must therefore be possible to characterize the above-mentioned relationship by the time-dependent behaviour of both the heat generation and the oxygen concentration. A number of complications impede the establishment of the relationship in this way.
Due to the high initial oxygen concentration in the sample vessel (up to 100%) the consumption of oxygen leads to large pressure variations in the course of the experiment. As a result of these large pressure variations physical processes such as evaporation tend to affect the relationship between the pressure and the heat generation considerably. In order to be able to interpret the IST experiments correctly throughout the entire experiment, i.e. even for large variations in the partial pressure of oxygen, two identical experiments have been carried out. A sample of coal type K3 was ground and stored under nitrogen. The coal sample was divided into two subsamples and transferred to two sample vessels. Then, both coal samples were stored in closed vessels under 100% oxygen at a temperature of 358 K. The heat generated by the coal in the first vessel was measured in the IST, whereas in the second vessel the pressure was carefully recorded throughout the degradation process of the coal. The result of both experiments is shown in Fig. 3.10. The logarithmic relation between the heat generation and the pressure (eq. 3.1) derived from both experiments is shown in Fig. 3.11. The power coefficient n in the logarithmic relation calculated from the experimental results is 1,7. This value of the power coefficient is abnormally high. This is due to the increasing difference between the total pressure and the

partial pressure of oxygen. When calculating the power coefficient n (= 1,7) both pressures were assumed to be equal. However, this appears not to be true. As a result of the temperature level of the experiment (358 K) and the considerable pressure variations the entire process is strongly affected by the evaporation of water in the closed vessel. This influence can be shown quickly and distinctly for two states, viz. the initial state and the final one.

The sample vessel (capacity 70 cm^3) was initially filled with dry oxygen under atmospheric pressure (100 kPa) at room temperature (298 K). A temperature increase up to 358 K leads theoretically to a pressure in the closed vessel of 120,3 kPa. However, the pressure measured in the experiment is 144 kPa. The deviation between both pressures can be imputed to the vapour pressure of water that is strongly increased at 358 K.

The ratio between the oxygen gas and the water vapour can be calculated because of the known amount of oxygen that is initially present in the sample vessel. The ratio at 358 K is

$$\frac{p_o}{p_w} = \frac{n_o}{n_w} = 5{,}076 \qquad (3.4)$$

Based on this ratio of the partial pressures of gas and vapour the amount of water that is evaporated is about 10 mg. The coal in the vessel weighed 5 g and had a moisture content of 7%. Hence the amount of water evaporated during the temperature increase amounts to about 30% of the moisture absorbed to the coal.

The vaporized amount of water can be obtained by cooling the sample vessel at the end of the experiment. In this experiment the vessel was quenched from 358 K down to 306 K leaving most of the vapour condensed. The gas phase at 306 K is saturated. From the saturation humidity (H_s = 0,0327), the overall pressure (13 kPa) and the temperature (306 K) the pressure ratio between gas and vapour can be calculated

$$\frac{p_o}{p_w} = \frac{n_o}{n_w} = 0{,}058 \qquad (3.5)$$

Using this ratio, the temperature decrease, and the unhampered condensation of the water vapour, it is apparent that at 358 K the ratio

must have been

$$\frac{p_o}{p_w} = \frac{n_o}{n_w} = 0{,}2638 \qquad (3.6)$$

This leads to a partial pressure of the water vapour p_w = 54,6 kPa and of oxygen gas p_o = 14,4 kPa. In this case the vaporized amount of water is approximately 23 mg, corresponding to 66% of the moisture initially absorbed to the coal (so excluding the water produced by the reaction). Therefore, the amount of water adsorbed to the coal is amply sufficient to control the evaporation throughout the experiment.

The evaporation process in the course of the experiment is less clearly structured and considerably less easy to be calculated. Proceeding from the amount of oxygen and water vapour present at the beginning and at the end of the experiment the partial pressures of the oxygen and the water vapour can be calculated as functions of time, using the time-dependent functions of the heat generation and the overall pressure. These calculations are based on the condition that the overall (measured) heat generation (q) is composed of the heat released by the reactions in the coal (q_o) and the heat needed to evaporate the water (q_w) according to the equation

$$q = q_o - q_w \qquad (3.7)$$

A further condition in this experiment is that at any moment the overall pressure consists entirely of the partial pressures of oxygen and of the water vapour. The time-dependent functions of the partial pressures of oxygen and water vapour calculated according to these two conditions appear to be complicated combinations of exponential equations. The time-dependent partial pressure of oxygen that is calculated in this way, is shown in Fig. 3.10 and Table 3.5

Table 3.5 Survey of the heat generation, the overall pressure and the partial pressure of oxygen during the degradation of coal type K3

Time (hr)	Heat generation (mW/kg)	Overall pressure (kPa)	Partial pressure of oxygen (kPa)
4	2250	122	98
6	1740	106	69
8	1445	95	53
12	1105	82	36

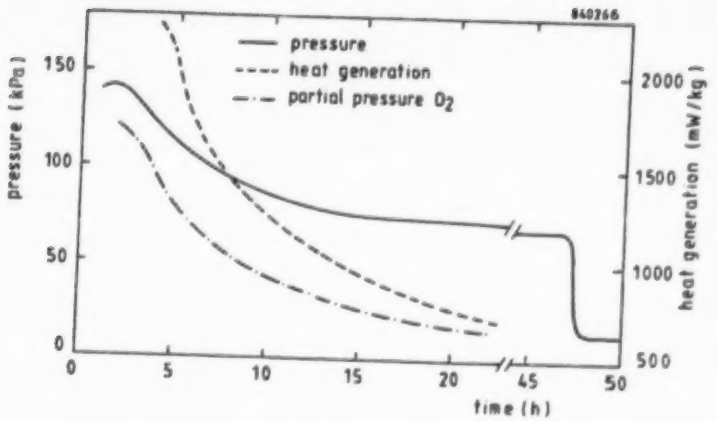

Fig. 3.10 Heat generation and pressure as functions of time during the isothermal degradation of coal type K3. The deviation between the pressure and the partial pressure of oxygen is almost entirely caused by the evaporation of water. (Arch.no. 840266)

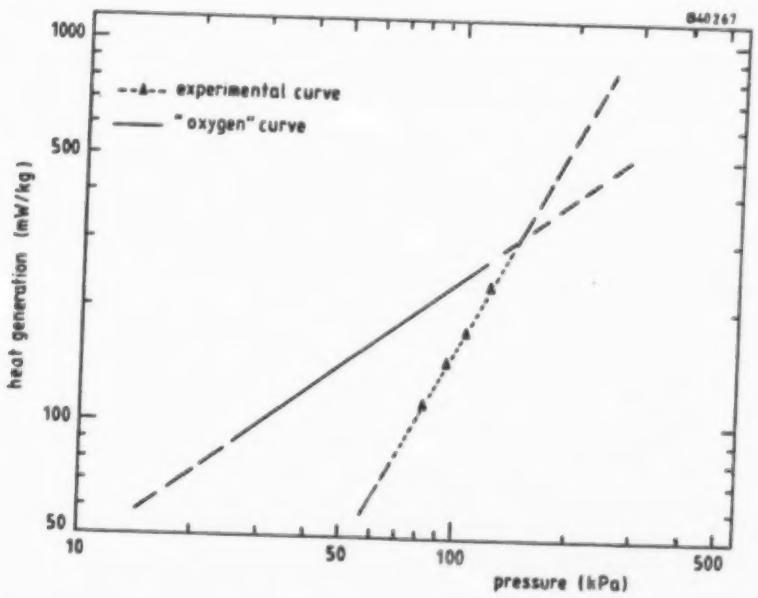

Fig. 3.11 Heat generation as a function of the overall pressure and the partial pressure of oxygen throughout the isothermal degradation of coal type K3. (Arch.no. 840267)

Compared to the relation between the heat generation and the (partial) pressure of oxygen as discussed at the beginning of this section a new relation has emerged with a power coefficient n equal to 0,73.
According to the isothermal measurements based on maximum heat generations this value appeared to be 0,7 and 0,77 using ranges of high and low partial pressures of oxygen, respectively. These values agree with one another within the experimental accuracies.
From these experiments it is obvious that the degradation of coal is dominated by two intertwined processes, the chemical process generating heat and the evaporative one needing heat. The parameters determining these processes can be obtained in the IST along various ways. The choice which set of experiments is to be performed depends on the kind of parameters and the accuracy necessary to describe the self-heating of the individual coal.

3.3 Adiabatic storage experiments

3.3.1 Introduction

The heat generation of the sub-bituminous coal of the types K4 and K5 has been measured under adiabatic conditions for various flow rates of the air through the coal.
The results of the adiabatic measurements performed in 1982 (4) proved that the behaviour of the moisture in the coal was an important factor in the self-heating process of the coal. In view of these measurements the theoretical model (2) was extended with a part in which the behaviour of the moisture was described.
The investigations performed in 1983 clearly confirm that only two processes dominate the self-heating of the coal, i.e. the chemical process in which the coal is oxidized and the physical process in which moisture is either evaporated or condensed. Both processes more or less oppose one another and depend on the local conditions in a coal pile. At a temperature of about 353-358 K the humidity of saturated air is such that in general an equilibrium is reached between the heat generated by the chemical reactions and the heat needed for the evaporation process. As long as some moisture remains in the heated area the coal will retain this temperature. As soon as the air cannot be saturated any longer by the insufficient moisture content of the coal a remarkably fast temperature rise is to be expected.

A further consequence of the evaporation is that the air in the hot area becomes saturated. In the temperature range of about 355 K the humidity of the saturated air strongly varies with the temperature. The temperature of the coal decreases downstream the hot area, which eventually leads to condensation of the excess of water in the air and, consequently to a temperature increase on account of the condensation. In this way a fairly good additional transport of heat is accomplished through the coal. Hence, an airflow ventilation through the coal influences the self-heating process twofold as both the amount of oxygen available for the chemical process and the humid phase transition process are affected.

3.3.2 The adiabatic saturation temperature

In the adiabatic process the heat needed to evaporate moisture into an airflow is provided by the coal itself (7). This results in a decrease in temperature of the coal. The influence of the flow rate of the air on this effect has been investigated with coal type K4. The behaviour of both the temperature and the water removal as a function of time and ventilation rate is shown in Fig. 3.12. In the first and second phase the removal of water is completely governed by the flow rate and the temperature.

The maximum amount of water which can be removed (5) (shown in Fig. 3.12) is 21 g during phase I and 11 g during phase II. The amount of water removed from the coal was condensed and weighed regularly. This amount appeared to be 20,7 g and 10,4 g for the phases I and II, respectively. The theoretical and the experimental values are in good agreement taking into account the accuracy of the measurements and the calculations. Coal type K4 contained 7,2 % of water. The adiabatic reaction vessel contained 0,6844 kg of coal and consequently 49,3 g of water. During phase III the coal is expected to have dried almost completely. From this point of time the airflow becomes unsaturated. Such a situation will be achieved at the point of time of approximately 230 hours. Until this moment the theoretical maximum amount of water that can be removed during phase III is 18 g. This leads to an average water removal of 78 g per m^3 of air ventilated through the coal in the period between 200 and 360 hours. The amount of water experimentally removed in this period appeared to be 68,1 g per m^3 of air. Taking into account the fairly rough estimates for

both the percentage of moisture in the coal and the original humidity of the air the amounts of water removed theoretically and experimentally compare favourably. So much for the behaviour of the moisture content of the coal.

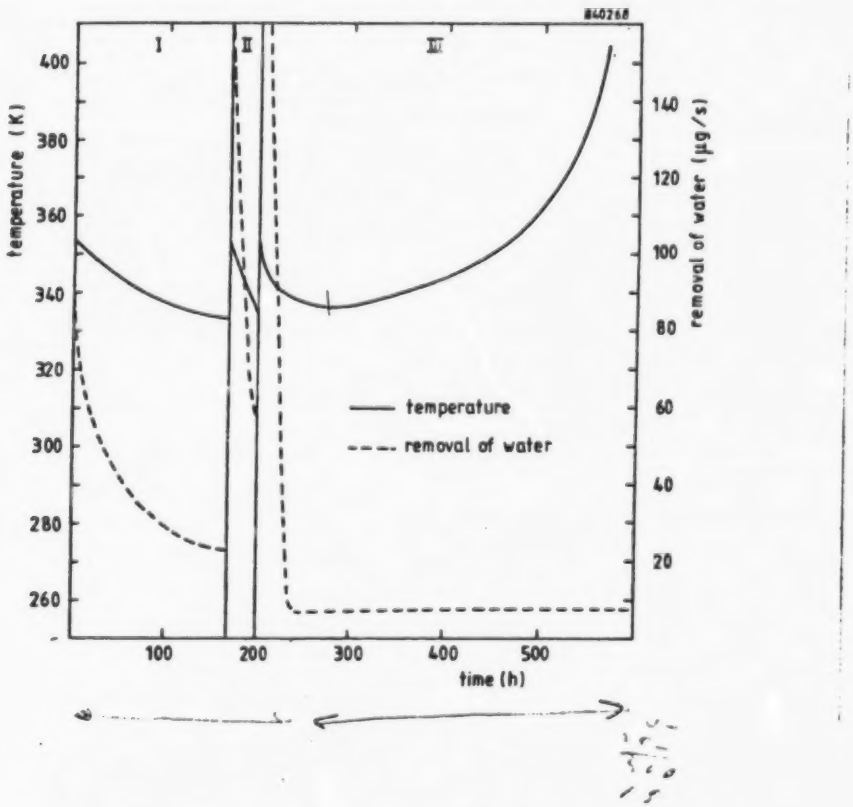

Fig. 3.12 Course of temperature and water removal of adiabatically stored coal (type K4) as functions of ventilation rate and time

phase I : flow rate 0,5 l/hr
phase II : flow rate 1,0 l/hr
phase III : flow rate 1,5 l/hr

(Arch.no. 840268)

The temperature history in the three phases is in good agreement with the behaviour of the removal of moisture. The decrease in temperature is determined by the heat needed for the evaporation of water. Superposed on the energy loss by evaporation is the energy generated by the chemical reaction processes in the coal. For the conditions that were chosen (flow rate, temperature, etc.) the energy loss exceeds the energy generation, resulting in an overall decrease in temperature.

This temperature decrease will continue until the energy generated is in balance with the energy necessary for the evaporation. The temperature thus obtained is similar to the adiabatic saturation temperature (7). The temperature in the reaction vessel will approach the adiabatic saturation temperature (ADST) exponentially, a phenomenon that was found experimentally in phase I. At the beginning of phase II the coal has been reheated up to a temperature of 353 K. Due to the increased flow rate another (lower) ADST will be approached. In phase III the coal has been reheated again up to 353 K and the increased flow rate necessitates the approach of a even lower ADST. Experiment and theory are in good agreement according to the initial declinations in the curves of temperature versus time in both phases.
As a result of the depletion of water the ADST gradually starts to increase until the coal is nearly dry. From this moment onwards the behaviour of the temperature is mainly determined by the heat generated by the coal reaction and the total heat capacity of the reaction vessel.

3.3.3 Oxygen depletion in the AST

The effect of oxygen on the heat generation has already been discussed in the isothermal storage test. It was shown that towards the end of the experiment the reaction was completely determined by the degree of depletion of oxygen.
In the AST the air flows freely through a column of coal. Throughout the column an oxidation reaction takes place with an intensity which depends on the local temperature and oxygen concentration. As oxygen is consumed by the reaction different oxygen concentrations may occur at both ends of the coal column, which leads to an undesired decrease in the average activity measured in the coal.
In order to quantify the effect of the variable oxygen concentration this concentration was measured by means of gas chromatography at both the inlet and outlet of the AST. The results of these measurements are shown in Fig. 3.13.

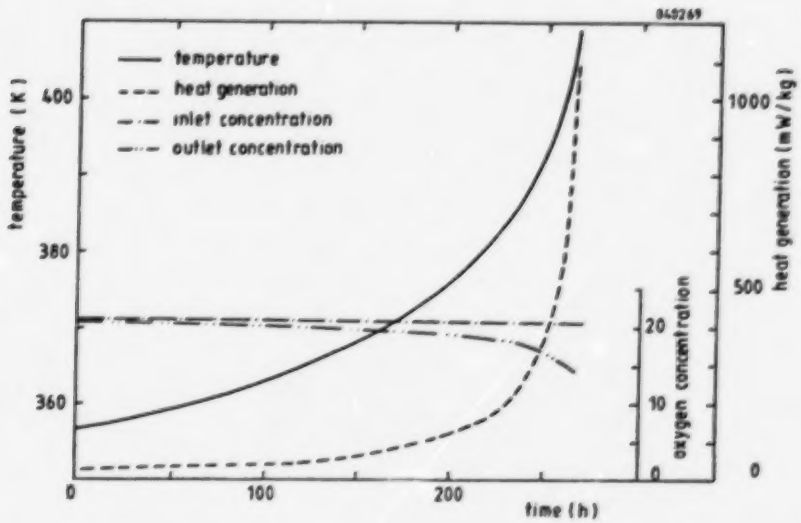

Fig. 3.13 Heat generation, temperature and oxygen concentrations of inlet and outlet gas flows as functions of time
(Arch.no. 840269)

It appears that only in the last phase of the experiments at temperatures well above 380 K a substantial decrease in the oxygen concentration is encountered using a flow rate of 1,5 l/hr. Also in this phase an increasing amount of water produced by the reaction is removed from the coal. The increased water removal is in agreement with the IST experiments in which decreases in pressure (by oxygen consumption) were followed by evaporation.

With a flow rate of 1,5 l/hr the difference in concentrations is 2,1 % and 6,0 % at temperatures of 385 K and 405 K, respectively. This leads to an hourly oxygen consumption of approximately 1,4 mmol at 385 K and of 4,0 mmol at 405 K. From these calculations it appears that at a rate of 1,5 l/hr the oxygen depletion increases from 10% at 385 K to 30% at 405 K.

Reduction of the flow rate leads to an even stronger depletion of oxygen. If the oxygen consumption is assumed to be only temperature-dependent the depletion at the same temperatures for a flow rate of 0,5 l/hr increases to 6,3 % and 17,9 %, respectively. Under such circumstances the decrease in reaction rate caused by oxygen depletion is evident.

At higher flow rates the substantial decrease in reaction rate shifts

3.3.4 Ventilation flow rates in the AST

The effect of the flow rate of the air on the heat generation and consequently on the temperature rise in the AST has been investigated with the coal types K4 and K5. The results of the experiments are shown in Fig. 3.14 and 3.15, respectively. In all experiments use was made of pre-dried coal. Therefore, all water additionally removed from the coal is produced by the reaction.

In the case of coal type K4 it appears that the adiabatic induction time (ADIND time) between the temperature levels of 358 K and 400 K varies from 100 up to 150 hours (upper curves). In this case the ADIND time increases with increasing ventilation rate. However, the increase in time is not gradual. In the case of coal type K5 the induction between 358 K and 400 K needs approximately 120 up to 170 hours (upper curves). Here, too, the ADIND time roughly increases for increasing ventilation flow rates, though again not gradually.

In general, four sources of disturbances appear to be responsible for the variation in ADIND times.

The first source is found at the starting-point of the ADIND process. By comparing the ADIND times one assumes all experiments to be similarly conditioned and at an equal temperature. In practice this is only roughly the case. Deviations in the starting conditions (less than 0,2 K) tend to grow in the self-heating process. However, the variations are not only due to this source.

The second source for the deviating behaviour is the evaporation of moisture. In all experiments the amount of water evaporated from the coal showed large variations (see the lower curves in Figs. 3.14 and 3.15). Because of the evaporation the energy released is only partly used in the self-heating process, thus delaying the temperature increase. Generally, the experiments with the longest ADIND times coincide with the highest evaporation rates.

The variations in the evaporation of moisture appeared to be dependent on the starting conditions, i.e. on the amount of water that remains in the coal after completion of the drying process, and on oscillations which appears to be a third source causing deviations. Depending on the flow rate, the air humidity and the (local) temperature in the column of coal oscillations may arise in a part of the column showing alternative condensation and evaporation of moisture as well as small variations in temperature. This phenomenon needs further experimental investigation. Because of the small oscillations in a part of the

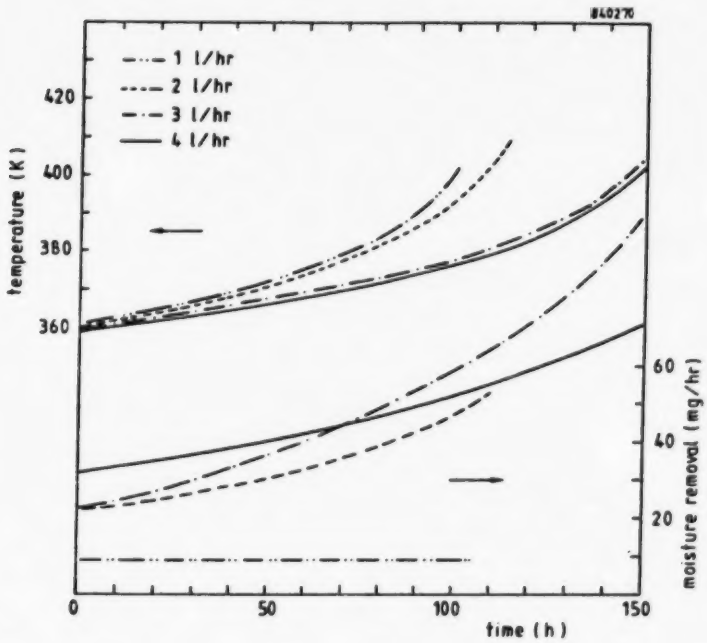

Fig. 3.14 Temperature and removal of water in the AST with coal type K4 as functions of time and flow rate (Arch.no. 840270)

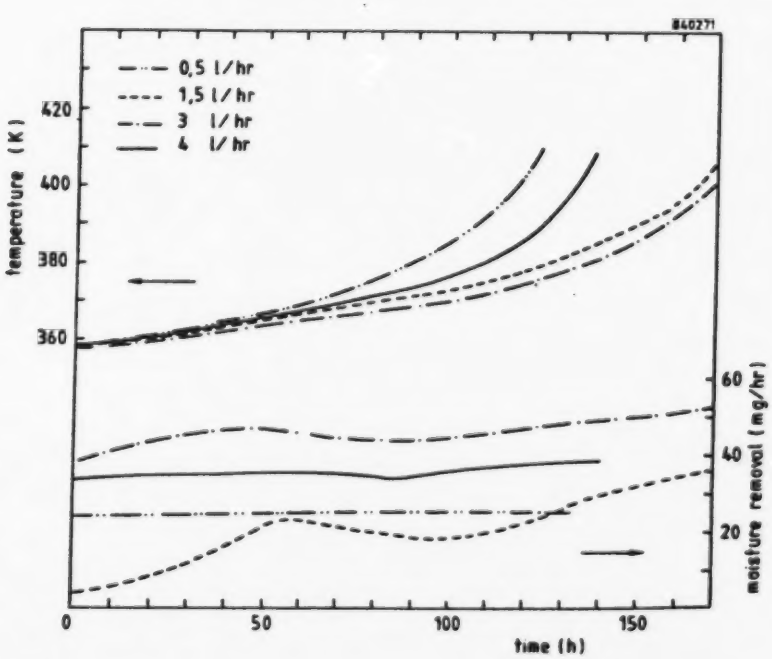

Fig. 3.15 Temperature and removal of water in the AST with coal

column deviations in the averaged ADIND times may occur. However, although they might influence the induction times, these oscillations will not influence the "overall" increase in temperature in the column. The fourth source of deviating behaviour depends on the oxygen depletion. As discussed in section 3.3.3 the depletion increases at low flow rates of the air and at increasing temperatures. Under the experimental conditions this effect is mainly encountered at the lower flow rates. Because of the oxygen depletion the reaction rate decreases and, hence, the ADIND time increases.

A comparison of the ADIND times of the coal types K4 and K5 reveals that the induction time of type K4 is somewhat shorter. This implicates a higher activity at these elevated temperatures. The implication agrees with the ratio of maximum heat generations (4). from which a similar conclusion was drawn.

4. CONCLUSIONS

The self-heating of coal comprises two major processes, viz. the exothermic oxidation reactions in the coal and the phase transition of water. The phase transition of water depends on the temperatures and moisture contents of the coal and gas phase which prevail locally in the coal. Therefore, the phase transition may be either the evaporation or the condensation of water. The temperature behaviour within the coal pile is the final result of these major processes.

The temperature behaviour is affected by a series of factors influencing either one or both major processes. The most important factors are the ventilation flow rate, the particle size, the degree of coal degradation, the partial pressure of oxygen, the moisture content of the coal, the porosity of the storage pile, the chemical composition of the coal and the storage time. Most of these factors are interrelated.

From the experiments performed during this study in 1983 it appears that the relation between the partial pressure of oxygen and the heat generation of the coal can be described by an exponential equation which is valid over the whole range of oxygen concentrations.

The decay in the caloric value of the coal obtained by long-term storage experiments rises to values between 4 and 6 % during the first year of storage. These losses are connected with the method of coal storage. The activity of the coal decreases with increasing storage periods. Further investigations are necessary to quantify the influence of the decreasing coal activity on the loss in caloric value for storage periods longer than one year.

The occurrence of chemicals in coal piles strongly affects the heat generation in the coal. Both sulphuric acid and ammonium hydroxide increase the heat generation by a factor of 2,5. The increased heat generation stimulates the local self-heating in the coal pile.

The influence of ventilation flow rates and oxygen depletion on the self-heating process has been investigated by means of the AST. The effect of the ventilation flow rate is complex. The oxidation reaction is stimulated by an increasing flow rate as a result of the additional supply of oxygen. Depending on the local temperature histories the amount of water adsorbed to the coal increases or decreases

at a faster rate by either evaporation or condensation. This causes an additional heat effect. Under these conditions a saturation temperature will be achieved which is bound up with the flow rate. The coal retains this saturation temperature as long as the coal remains moist. As soon as the moisture contents of the coal becomes too low and the air becomes unsaturated a remarkably fast temperature increase is to be expected. This behaviour leads to the suggestion that local hot areas in the coal may be extinguished by injecting relatively small amounts of water in or close to the hot spot (downstream with respect to the direction of the airflow) in combination with a simultaneous increase in the airflow rate. Additional experiments are necessary to substantiate this suggestion.

Concerning the oxygen depletion it appeared that only at relatively low flow rates and at relatively high temperatures (only occurring if the reaction process is well-advanced) substantial decreases in the oxygen concentration are encountered in the airflow.

In general, all experiments performed until now proved that the self-heating of coal is a result of the two major processes mentioned above. The parameters in these processes can be established by IST and AST experiments. The temperature history of all points in the coal pile can be obtained with the aid of a model that is capable of describing these two processes simultaneously.

5. RECOMMENDATIONS

The continuation of the long-term storage tests of coal is necessary in order to quantify the caloric losses and the decrease in activity of the coal as a consequence of this storage.

Furthermore, the quantification of the oscillating behaviour of the temperature and the water concentration in a column of coal ventilated by air (e.g. such as used in the AST) is needed experimentally and theoretically by local temperature registration, moisture content determination and model verification.

It is recommended to substantiate with experiments a method of fire extinguishing by injecting a relatively small amount of water into the hot spot combined with a simultaneous forced airflow.

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ANNEX I

Proximate analysis of coal sample K3

Serial number of the coal	K3
Coal type	sub-bituminous
Origin	Australia
Storage position	Amercentrale, pile 6AN, new
Volatiles	26,02 %
Ash content	10,13 %
Moisture of the coal	12,75 %
Carbon content	51,10 %
Caloric value	24,95 $MJ.kg^{-1}$

ANNEX II

Proximate analysis of coal sample K4

Serial number of the coal	K4
Coal type	sub-bituminous
Origin	Australia
Storage position	Amercentrale
Volatiles	22,16 %
Ash content	16,68 %
Moisture of the coal	7,41 %
Carbon content	53,75 %
Caloric value	25,41 $MJ.kg^{-1}$

ANNEX III

Proximate analysis of coal sample K5

Serial number of the coal	K5
Coal type	sub-bituminous
Origin	U.S.A.
Storage position	PGEM
Volatiles	32,25 %
Ash content	5,77 %
Moisture of the coal	8,67 %
Carbon content	53,31 %
Caloric value	28,36 $MJ.kg^{-1}$

SUMMARY:

The results of the investigation into the heat generation of coal which has been performed under contract with BEOP, are collected in this report. The relationship between the heat generation and the partial pressure of oxygen has been investigated for low oxygen concentrations (0-20% O_2). An unequivocal relationship could be established, which is in agreement with the observations at high oxygen concentrations (10-100% O_2).
The loss in caloric values and in the activity of the coal has been established with long-term storage experiments performed at 305 and 323 K. It appears that the addition of such chemicals as sulphuric acid and iron salts that are frequently encountered in coal piles stimulate the heat generation.
Adiabatic investigation reveal an equilibrium between the moisture in the gas phase and in the solid phase, leading to an adiabatic saturation temperature. This temperature is dependent on the flow rate and appears to remain between 348 and 363 K under normal storage conditions.
It is evident from all experiments that the entire process of self-heating is determined by the chemical oxidation process generating heat and the physical process of evaporation consuming heat.

SAMENVATTING

In dit rapport zijn de resultaten gebundeld van het in opdracht van BEOP uitgevoerde onderzoek naar de warmteproduktie van steenkool.
Onderzocht is de invloed van de zuurstofconcentratie op de warmteproduktie in de kool bij lage zuurstofconcentraties (0-20% O_2). Een eenduidige relatie kon worden vastgesteld die aansluit bij de waarnemingen bij hoge zuurstofconcentraties (20-100% O_2).
Het verlies in stookwaarde en de teruggang in activiteit van de kool is vastgesteld via proeven aan een langdurige opslag van de kool bij 305 en 323 K. Tevens is vastgesteld dat de aanwezigheid van enkele regelmatig bij koolopslag voorkomende stoffen als zwavelzuur en ijzer, de warmteproduktie beïnvloedt.
Uit adiabatisch onderzoek blijkt dat het doorleiden van lucht leidt tot een evenwicht tussen het vocht in de gas- en vaste fase bij een adiabatische verzadigingstemperatuur. Deze temperatuur, die afhankelijk is van het debiet van de gasstroom blijkt bij normale opslagcondities ongeveer 348-363 K te zijn.
Uit de metingen blijkt duidelijk dat het broeiproces geheel wordt bepaald door een warmteproducerend proces (de exotherme oxidatie van kool) en een proces dat warmte kost (de verdamping van water).

Prins Maurits Laboratorium TNO

Report no.:

Assignment no(s): M9189

Date: February 13th, 1984

Title: Self-heating of sub-bituminous coal
- investigations 1983 -

Author: dr. A.H. Heemskerk

Descriptor(s):

coal storage	0809
coal	0807
coal	2104
thermal stability	2013
thermodynamic properties	2013
heat measurement	1402
degradation	1407

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